3.17. Perturbation Expansion of Anharmonic Systems

In this section, we develop the formal perturbation theory, which is numerically strongly divergent except for extremely weak perturbations. A theory with better convergence that combines both perturbation & variational approaches will be developed in chapter 5.

Consider then the quantum-mechanical amplitude

$$(x_b\, t_b \mid x_a\, t_a) = \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\, x\, e^{i\mathcal{A}/\hbar} \tag{3.473}$$

$$\mathcal{A} = \int_{t_a}^{t_b} d\,t\, L \tag{3.473a}$$

$$L = \frac{1}{2} M\, \dot{x}^2 - \frac{1}{2} M\, \omega^2\, x^2 - V(x) \tag{3.473b}$$

where the anharmonic potential V is the perturbation.

Using

$$L = L_0 - V \qquad\qquad L_0 = \frac{1}{2} M\, \dot{x}^2 - \frac{1}{2} M\, \omega^2\, x^2 \tag{3.473c}$$

we can write

$$\mathcal{A} = \mathcal{A}_0 + \mathcal{A}_{\text{int}} \tag{3.473d}$$

where

$$\mathcal{A}_0 = \int_{t_a}^{t_b} d\,t\, L_0 \qquad\qquad \mathcal{A}_{\text{int}} = -\int_{t_a}^{t_b} d\,t\, V[x(t)] \tag{3.473e}$$

The exponential can be formally expanded as

$$\begin{aligned} e^{i\mathcal{A}/\hbar} &= e^{i\mathcal{A}_0/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i}{\hbar}\right)^n \mathcal{A}_{\text{int}}^n \\ &= \exp\left\{ \frac{i}{\hbar} \int_{t_a}^{t_b} d\,t \left[\frac{1}{2} M\, \dot{x}^2 - \frac{1}{2} M\, \omega^2\, x^2 \right] \right\} \\ &\quad \times \left\{ 1 - \frac{i}{\hbar} \int_{t_a}^{t_b} d\,t_1\, V[x(t_1)] + \frac{1}{2!} \left(\frac{i}{\hbar}\right)^2 \int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_b} d\,t_1\, V[x(t_2)]\, V[x(t_1)] \right. \\ &\quad \left. - \frac{1}{3!} \left(\frac{i}{\hbar}\right)^3 \int_{t_a}^{t_b} d\,t_3 \int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_b} d\,t_1\, V[x(t_3)]\, V[x(t_2)]\, V[x(t_1)] + \ldots \right\} \end{aligned} \tag{3.474}$$

Setting

$$\begin{aligned} (x_b\, t_b \mid x_a\, t_a)_0 &= \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\, x\, e^{i\mathcal{A}_0/\hbar} \\ &= \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\, (x_b\, t_b \mid x_1\, t_1)_0\, (x_1\, t_1 \mid x_a\, t_a)_0 \end{aligned}$$

(3.473-4) can be written as

$$\begin{aligned} &(x_b\, t_b \mid x_a\, t_a) \\ &= (x_b\, t_b \mid x_a\, t_a)_0 - \frac{i}{\hbar} \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\, (x_b\, t_b \mid x_1\, t_1)_0\, V(x_1)\, (x_1\, t_1 \mid x_a\, t_a)_0 \\ &\quad + \frac{1}{2!} \left(\frac{i}{\hbar}\right)^2 \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\, (x_b\, t_b \mid x_2\, t_2)_0 \\ &\quad * V(x_2)\, (x_2\, t_2 \mid x_1\, t_1)_0\, V(x_1)\, (x_1\, t_1 \mid x_a\, t_a)_0 + \ldots \end{aligned} \tag{3.475}$$

Similarly, the partition function is related to the Euclidean version of (3.473a-e) as

$$Z = \oint \mathcal{D}\, x\, e^{-\mathcal{A}_e/\hbar} \tag{4.476}$$

$$\mathcal{A}_e = \int_0^{\beta\hbar} d\tau\, L_e \tag{3.476a}$$

$$L_e = \frac{1}{2} M \dot{x}^2 + \frac{1}{2} M \omega^2 x^2 + V(x) \tag{3.476b}$$

Using

$$L_e = L_{0,e} + V \qquad L_{0,e} = \frac{1}{2} M \dot{x}^2 + \frac{1}{2} M \omega^2 x^2 \tag{3.476c}$$

we can write

$$\mathcal{A}_e = \mathcal{A}_{0,e} + \mathcal{A}_{\text{int},e} \tag{3.476d}$$

where

$$\mathcal{A}_{0,e} = \int_0^{\beta\hbar} d\tau\, L_{0,e} \qquad \mathcal{A}_{\text{int},e} = \int_0^{\beta\hbar} d\tau\, V[x(\tau)] \tag{3.478}$$

$$e^{-\mathcal{A}_e/\hbar} = e^{-\mathcal{A}_{0,e}/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar}\right)^n \mathcal{A}_{\text{int},e}^n$$

$$= \exp\left\{-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left[\frac{1}{2} M \dot{x}^2 + \frac{1}{2} M \omega^2 x^2\right]\right\} \tag{3.477}$$

$$\times \left\{1 - \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau_1\, V[x(\tau_1)] + \frac{1}{2!\,\hbar^2} \int_0^{\beta\hbar} d\tau_2 \int_0^{\beta\hbar} d\tau_1\, V[x(\tau_2)]\, V[x(\tau_1)] \right.$$

$$\left. - \frac{1}{3!\,\hbar^3} \int_0^{\beta\hbar} d\tau_3 \int_0^{\beta\hbar} d\tau_2 \int_0^{\beta\hbar} d\tau_1\, V[x(\tau_3)]\, V[x(\tau_2)]\, V[x(\tau_1)] + \ldots \right\}$$

Setting

$$Z_\omega = \oint \mathcal{D} x\, e^{-\mathcal{A}_{0,e}/\hbar} \tag{3.479a}$$

and

$$\langle F \rangle_\omega = \frac{1}{Z_\omega} \oint \mathcal{D} x\, e^{-\mathcal{A}_{0,e}/\hbar}\, F \tag{3.479}$$

(4.476-7) give

$$Z = Z_\omega \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar}\right)^n \langle \mathcal{A}_{\text{int},e}^n \rangle_\omega \tag{3.480}$$

The cumulant expansion re-writes (3.476d) as

$$\mathcal{A}_e = \mathcal{A}_{0,e} + \langle \mathcal{A}_{\text{int},e} \rangle_\omega + \Delta\mathcal{A}_{\text{int},e} \tag{3.480a}$$

where

$$\Delta\mathcal{A}_{\text{int},e} = \mathcal{A}_{\text{int},e} - \langle \mathcal{A}_{\text{int},e} \rangle_\omega \tag{3.480b}$$

$$\rightarrow \qquad e^{-\mathcal{A}_e/\hbar} = \exp\left[-\frac{1}{\hbar}\left(\mathcal{A}_{0,e} + \langle \mathcal{A}_{\text{int},e} \rangle_\omega\right)\right] \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar}\right)^n \Delta\mathcal{A}_{\text{int},e}^n \tag{3.480c}$$

(3.480) thus becomes

$$Z = Z_\omega\, e^{-\langle \mathcal{A}_{\text{int},e} \rangle_\omega/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar}\right)^n \langle \mathcal{A}_{\text{int},e}^n \rangle_{\omega,c} \tag{3.481}$$

where the cumulants are defined as

$$\langle \mathcal{A}_{\text{int},e}^n \rangle_{\omega,c} \equiv \langle \Delta\mathcal{A}_{\text{int},e}^n \rangle_\omega \tag{3.481a}$$

$$= \left\langle \left(\mathcal{A}_{\text{int},e} - \langle \mathcal{A}_{\text{int},e} \rangle_\omega\right)^n \right\rangle_\omega$$

For example,

$$\langle \mathcal{A}_{\text{int},e} \rangle_{\omega,c} \equiv \left\langle \left(\mathcal{A}_{\text{int},e} - \langle \mathcal{A}_{\text{int},e} \rangle_\omega\right) \right\rangle_\omega = 0 \tag{3.481b}$$

$$\left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega,\,c} \equiv \left\langle \left(\mathcal{A}_{\text{int},e} - \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} \right)^{2} \right\rangle_{\omega}$$
$$= \left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega} - \langle \mathcal{A}_{\text{int},e} \rangle_{\omega}^{2} \tag{3.482}$$

$$\left\langle \mathcal{A}_{\text{int},e}^{3} \right\rangle_{\omega,\,c} \equiv \left\langle \left(\mathcal{A}_{\text{int},e} - \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} \right)^{3} \right\rangle_{\omega}$$
$$= \left\langle \mathcal{A}_{\text{int},e}^{3} \right\rangle_{\omega} - 3 \left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} + 3 \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega}^{2} - \langle \mathcal{A}_{\text{int},e} \rangle_{\omega}^{3}$$
$$= \left\langle \mathcal{A}_{\text{int},e}^{3} \right\rangle_{\omega} - 3 \left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} + 2 \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega}^{2} \tag{3.483}$$

& so on.

The change in the free energy is

$$\Delta F = -\frac{1}{\beta} \ln \frac{Z}{Z_{\omega}}$$
$$= -\frac{1}{\beta} \left\{ -\frac{1}{\hbar} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} + \ln \left[\sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar} \right)^{n} \langle \mathcal{A}_{\text{int},e}^{n} \rangle_{\omega,c} \right] \right\}$$
$$= \frac{1}{\beta} \left\{ \frac{1}{\hbar} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} - \ln \left[1 + \sum_{n=2}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar} \right)^{n} \langle \mathcal{A}_{\text{int},e}^{n} \rangle_{\omega,c} \right] \right\}$$

Using

$$\ln \left(1 + \sum_{i} x_i \right) = \sum_{i} x_i - \frac{1}{2} \left(\sum_{i} x_i \right)^{2} + \frac{1}{3} \left(\sum_{i} x_i \right)^{3} - \ldots$$

we have

$$\Delta F = \frac{1}{\beta} \left\{ \frac{1}{\hbar} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} - \frac{1}{2!\,\hbar^{2}} \left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega,c} + \frac{1}{3!\,\hbar^{3}} \left\langle \mathcal{A}_{\text{int},e}^{3} \right\rangle_{\omega,c} + \ldots \right\} \tag{3.484}$$

The ground state energy shift is therefore

$$\Delta E_0 = \lim_{\beta \to \infty} \frac{1}{\beta} \left\{ \frac{1}{\hbar} \langle \mathcal{A}_{\text{int},e} \rangle_{\omega} - \frac{1}{2!\,\hbar^{2}} \left\langle \mathcal{A}_{\text{int},e}^{2} \right\rangle_{\omega,c} + \frac{1}{3!\,\hbar^{3}} \left\langle \mathcal{A}_{\text{int},e}^{3} \right\rangle_{\omega,c} + \ldots \right\} \tag{3.485}$$

For a monotonic potential V that doesn't change sign in the interval $(0, \beta \hbar)$,

$$\mathcal{A}_{\text{int},e} = \int_{0}^{\beta \hbar} d\tau \; V[x(\tau)] \; \propto \beta \hbar$$
$$\mathcal{A}_{\text{int},e}^{n} \propto (\beta \hbar)^{n} \qquad \to \qquad \langle \mathcal{A}_{\text{int},e}^{n} \rangle_{\omega} \propto (\beta \hbar)^{n}$$

However

$$\langle \mathcal{A}_{\text{int},e} \rangle_{\omega,\,c} = 0$$

so that $\langle \mathcal{A}_{\text{int},e}^{n} \rangle_{\omega,\,c}$ depends on $\beta \hbar$ weakly. If ΔE_0 is to be finite, then $\langle \mathcal{A}_{\text{int},e}^{n} \rangle_{\omega,\,c} \propto \beta \hbar$.

The perturbation expansion of Z can also be obtained from the functional derivatives of

$$Z[j] = \oint \mathcal{D} x \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_{e}[j] \right\} \tag{3.486}$$

where

$$\mathcal{A}_{e}[j] = \int_{0}^{\beta \hbar} d\tau \left[\frac{1}{2} M \dot{x}^{2} + \frac{1}{2} M \omega^{2} x^{2} + V(x) - j x \right] \tag{3.486a}$$

We can write

$$Z[j] = \exp \left\{ -\frac{1}{\hbar} \int_{0}^{\beta \hbar} d\tau \, V \left[\frac{\delta}{\delta j(\tau)} \right] \right\} Z_{\omega}[j] \tag{3.487}$$

where

$$Z_{\omega}[j] = \oint \mathcal{D} x \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_{0,\,e}[j] \right\} \tag{3.489}$$

$$\mathcal{A}_{0,e}[j] = \frac{1}{2} M \dot{x}^2 + \frac{1}{2} M \omega^2 x^2 - j x \tag{3.489a}$$

The quantity of interest is of course

$$Z = Z[0] \tag{3.488}$$

(3.487) suggests the series expansion

$$\begin{aligned} &\exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, V\left[\frac{\delta}{\delta j(\tau)}\right]\right\} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!}\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, V\left[\frac{\delta}{\delta j(\tau)}\right]\right\}^n \\ &= 1 - \frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, V\left[\frac{\delta}{\delta j(\tau)}\right] \\ &\quad + \frac{1}{2!\,\hbar^2}\int_0^{\beta\hbar} d\tau_2 \int_0^{\beta\hbar} d\tau_1\, V\left[\frac{\delta}{\delta j(\tau_2)}\right] V\left[\frac{\delta}{\delta j(\tau_1)}\right] \\ &\quad - \frac{1}{3!\,\hbar^3}\int_0^{\beta\hbar} d\tau_3 \int_0^{\beta\hbar} d\tau_2 \int_0^{\beta\hbar} d\tau_1\, V\left[\frac{\delta}{\delta j(\tau_3)}\right] V\left[\frac{\delta}{\delta j(\tau_2)}\right] V\left[\frac{\delta}{\delta j(\tau_1)}\right] + \ldots \end{aligned} \tag{3.490}$$

Carrying out the functional derivatives explicitly, we recover (3.480).

Finally, we mention that the partition function [see (4.476)]

$$Z = \oint \mathcal{D} x\, e^{-\mathcal{A}_e/\hbar}$$

can also serves as the generating function for $\langle \mathcal{A}_e^n \rangle$.

From (2.62),

$$\oint \mathcal{D} x = \lim_{N\to\infty}\left(\prod_{k=1}^{N+1}\left(\frac{M}{2\pi i \hbar \epsilon}\right)^{1/2}\int d x_k\right)_{x_b = \mathbf{x_a}}$$

we see that the measure is also dependent on $\hbar^{-1}$.   However, this dependence is cancelled out for

$$\frac{1}{Z}\oint \mathcal{D} x$$

Therefore, we have

$$\begin{aligned} \langle \mathcal{A}_e^n \rangle &= \frac{1}{Z}\oint \mathcal{D} x\, \mathcal{A}_e^n\, e^{-\mathcal{A}_e/\hbar} \\ &= (-)^n \frac{1}{Z}\frac{\partial^n Z}{\partial\left(\hbar^{-1}\right)^n}\bigg|_{\hbar^{-1}=0} \end{aligned} \tag{3.491}$$

For a harmonic oscillator with partition function [see (3.242)]

$$Z_\omega = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

we have

$$\begin{aligned} \langle \mathcal{A} \rangle &= -\frac{1}{Z_\omega}\hbar^2 \frac{\partial}{\partial \hbar} Z_\omega\bigg|_{\hbar^{-1}=0} \\ &= -\hbar^2 \frac{\partial}{\partial \hbar}\ln Z_\omega\bigg|_{\hbar^{-1}=0} \\ &= \hbar^2 \frac{1}{\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}\frac{1}{2}\beta\omega\cosh\left(\frac{1}{2}\beta\hbar\omega\right)\bigg|_{\hbar^{-1}=0} \end{aligned}$$

$$= \frac{1}{2} \beta \hbar^2 \omega \coth\left(\frac{1}{2} \beta \hbar \omega\right) \Big|_{\hbar^{-1}=0} \qquad (3.492a)$$

$\to \infty$

On the other hand,

$$\langle \mathcal{A} \rangle = \frac{1}{2} M \int_0^{\beta\hbar} d\tau \left[\langle \dot{x}^2 \rangle + \omega^2 \langle x^2 \rangle \right]$$

$$= \frac{1}{2} \int_0^{\beta\hbar} d\tau \left[\hbar \delta(0) - \frac{1}{M} \langle p^2 \rangle + M \omega^2 \langle x^2 \rangle \right] \qquad \text{[(3.352) used.]}$$

$$= \frac{1}{2} \int_0^{\beta\hbar} d\tau \left[\hbar \delta(0) - \frac{1}{M} G^{(2)}_{\omega^2, pp}(\tau, \tau) + M \omega^2 G^{(2)}_{\omega^2, xx}(\tau, \tau) \right]$$

$$= \frac{1}{2} \hbar \int_0^{\beta\hbar} d\tau \left[\delta(0) + \left(-\omega^2 + \omega^2\right) G^{p}_{\omega^2, e}(\tau, \tau) \right] \qquad \text{[(3.346-9) used]}$$

$$= \frac{1}{2} \beta \hbar^2 \delta(0) \qquad (3.493)$$

$$= \frac{1}{2} \beta \hbar^2 \int \frac{d\omega}{2\pi}$$

$$= 0 \qquad \text{[Veltman's rule (2.506) used.]} \qquad (3.493)$$

Thus, (3.492a) agrees with (3.493) but disagrees with (3.493).

Note that

$$\langle H \rangle = \frac{1}{2} \int_0^{\beta\hbar} d\tau \left[\frac{1}{M} \langle p^2 \rangle + M \omega^2 \langle x^2 \rangle \right]$$

$$= \hbar \omega^2 \int_0^{\beta\hbar} d\tau \, G^{p}_{\omega^2, e}(\tau, \tau)$$

$$= \hbar \omega^2 \int_0^{\beta\hbar} d\tau \frac{\cosh\left(\frac{1}{2} \beta \hbar \omega\right)}{2 \omega \sinh\left(\frac{1}{2} \beta \hbar \omega\right)} \qquad \text{[(3.219) used.]}$$

$$= \frac{1}{2} \beta \hbar^2 \omega \coth\left(\frac{1}{2} \beta \hbar \omega\right) \qquad (3.493a)$$