3.18. Rayleigh-Schrodinger and Brillouin-Wigner Perturbation Expansion

The expectation values in the partition function expression (3.480) can be evaluated by means of the so-called Rayleigh-Schrodinger (or old-fashioned) perturbation expansion.

For example, the free energy shift ΔF in (3.484) requires the calculations of

$$\langle \mathcal{A}_{\text{int},e} \rangle_\omega \equiv \frac{1}{Z_\omega} \int d\,x \int_0^{\beta\hbar} d\,\tau_1 \int d\,x_1\,(\,x\,\beta\,\hbar\mid x_1\,\tau_1)_\omega\, V(x_1)\,(\,x_1\,\tau_1\mid x\,0\,)_\omega \qquad (3.494)$$

for the 1st order perturbation, and

$$\frac{1}{2}\langle \mathcal{A}^2_{\text{int},e} \rangle_\omega \equiv \frac{1}{Z_\omega} \int d\,x \int_0^{\beta\hbar} d\,\tau_2 \int d\,x_2 \int_0^{\tau_2} d\,\tau_1 \int d\,x_1 \qquad (3.495)$$

$$\times\,(\,x\,\beta\,\hbar\mid x_2\,\tau_2)_\omega\, V(x_2)\,(\,x_2\,\tau_2\mid x_1\,\tau_1)_\omega\, V(x_1)\,(\,x_1\,\tau_1\mid x\,0\,)_\omega$$

for the 2nd order perturbation. Note that we've made use of the fact that $\int_0^{\tau_2} d\,\tau_1$ & $\int_{\tau_2}^{\beta\hbar} d\,\tau_1$ give the same result in (3.495).

Consider now the expansion of the real-time evolution amplitude (3.475). With

$$\mathcal{A}_{\text{int}} = -\int_{t_a}^{t_b} d\,t\, V[x(t)] \qquad \text{[cf. (3.473e)]} \qquad (3.498)$$

and ($\mathcal{A}_0$ denoted as $\mathcal{A}_\omega$),

$$(x_b\,t_b\mid x_a\,t_a) = \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\,x\, e^{i\mathcal{A}_\omega/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{i}{\hbar}\right)^n \mathcal{A}^n_{\text{int}} \quad \text{[cf. (3.473-4)]} \quad (3.498a)$$

we have

$$\int d\,x_b \int d\,x_a\,(x_b\,t_b\mid x_a\,t_a)$$

$$= Z^{\text{open}}_{\text{QM},\,\omega}\left\{1 + \frac{i}{\hbar}\langle \mathcal{A}_{\text{int}}\rangle_\omega + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2 \left\langle \mathcal{A}^2_{\text{int}}\right\rangle_\omega + \frac{1}{3!}\left(\frac{i}{\hbar}\right)^3 \left\langle \mathcal{A}^3_{\text{int}}\right\rangle_\omega + \ldots\right\} \qquad (3.498b)$$

where

$$(x_b\,t_b\mid x_a\,t_a)_\omega = \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\,x\, e^{i\mathcal{A}_\omega/\hbar} \qquad (3.498c)$$

$$Z^{\text{open}}_{\text{QM},\,\omega} = \int d\,x_b \int d\,x_a\,(x_b\,t_b\mid x_a\,t_a)_\omega \qquad \text{[cf. } Z^{\text{open}}_\omega \text{ in §2.10.]}$$

$$= \int d\,x_b \int d\,x_a \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\,x\, e^{i\mathcal{A}_\omega/\hbar} \qquad (3.498d)$$

$$\langle f \rangle_\omega \equiv \frac{1}{Z^{\text{open}}_{\text{QM},\,\omega}} \int d\,x_b \int d\,x_a \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathcal{D}\,x\, e^{i\mathcal{A}_\omega/\hbar} f \qquad (3.498e)$$

Consider now the spectral expansion (2.298) for the harmonic oscillator

$$(x_b\,t_a\mid x_a\,t_a)_\omega = \sum_{n=0}^{\infty} \psi_n(x_b)\,\psi_n^*(x_a)\, e^{-i E_n(t_b - t_a)/\hbar} \qquad (3.507)$$

$$= \sum_{n=0}^{\infty} \langle\, x_b\mid n\,\rangle\langle\, n\mid x_a\,\rangle\, e^{-i E_n(t_b - t_a)/\hbar} \qquad (3.507a)$$

and its Euclidean version

$$(x_b\,\tau_a\mid x_a\,\tau_a)_\omega = \sum_{n=0}^{\infty} \psi_n(x_b)\,\psi_n^*(x_a)\, e^{-E_n(\tau_b - \tau_a)/\hbar} \qquad (3.496)$$

where the eigen-functions $\{\,\psi_n\,\}$ are assumed to be orthonormal, complete, and with eigen-energies

$$E_n = \hbar\,\omega\left(n + \frac{1}{2}\right) \tag{3.496c}$$

Then (3.496a) gives

$$\begin{aligned}(n\,;\,t_b,\,t_a)_\omega &\equiv \int d\,x_b \int d\,x_a\,\psi_n^*(x_b)\,(x_b\,t_a \mid x_a\,t_a)_\omega\,\psi_n(x_a)\\ &= \sum_{m=0}^{\infty}\int d\,x_b \int d\,x_a\,\psi_n^*(x_b)\,\psi_m(x_b)\,\psi_m^*(x_a)\,\psi_n(x_a)\,e^{-i E_m (t_b - t_a)/\hbar}\\ &= e^{-i E_n (t_b - t_a)/\hbar}\\ &\equiv Z_{\mathrm{QM},\,\omega,\,n}\end{aligned} \tag{3.500}$$

which is just the projection of $Z_{\mathrm{QM},\,\omega}$ onto the eigenstate ψ_n. Here

$$\begin{aligned}Z_{\mathrm{QM},\,\omega} &= \int d\,x\,(x\,t_a \mid x\,t_a)_\omega\\ &= \sum_{n=0}^{\infty}\int d\,x\;\langle n \mid x\rangle\langle x \mid n\rangle\,e^{-i E_n (t_b - t_a)/\hbar}\\ &= \sum_{n=0}^{\infty} e^{-i E_n (t_b - t_a)/\hbar}\end{aligned} \tag{3.500a}$$

is the quantum partition with periodic B.C.

Analogous to (3.498b), (3.498a) thus gives

$$\begin{aligned}(n\,;\,t_b,\,t_a) &\equiv \int d\,x_b \int d\,x_a\,\psi_n^*(x_b)\,(x_b\,t_b \mid x_a\,t_a)\,\psi_n(x_a)\\ &= Z_{\mathrm{QM},\,\omega,\,n}\left\{1 + \frac{i}{\hbar}\langle n \mid \mathcal{A}_{\mathrm{int}} \mid n\rangle_\omega + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2\left\langle n \mid \mathcal{A}_{\mathrm{int}}^2 \mid n\right\rangle_\omega\right.\\ &\qquad\left. + \frac{1}{3!}\left(\frac{i}{\hbar}\right)^3\left\langle n \mid \mathcal{A}_{\mathrm{int}}^3 \mid n\right\rangle_\omega + \ldots\right\}\end{aligned} \tag{3.497}$$

where

$$\langle n \mid f \mid n\rangle_\omega \equiv \frac{1}{Z_{\mathrm{QM},\,\omega,\,n}}\int d\,x_b \int d\,x_a\,\psi_n^*(x_b)\,\psi_n(x_a)\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathcal{D}\,x\,e^{i\mathcal{A}_\omega/\hbar} f \tag{3.499}$$

As in (3.494), we can break up the path integral by time-segments so that

$$\begin{aligned}\langle n \mid \mathcal{A}_{\mathrm{int}} \mid n\rangle_\omega &= -\frac{1}{Z_{\mathrm{QM},\,\omega,\,n}}\int d\,x_b \int d\,x_a \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\\ &\quad\times\psi_n^*(x_b)\,(\,x_b\,t_b \mid x_1\,t_1)_\omega\,V(x_1)\,(\,x_1\,t_1 \mid x_a\,t_a\,)_\omega\,\psi_n(x_a)\end{aligned} \tag{3.501}$$

Similarly,

$$\begin{aligned}\frac{1}{2}\left\langle n \mid \mathcal{A}_{\mathrm{int}}^2 \mid n\right\rangle_\omega &= \frac{1}{Z_{\mathrm{QM},\,\omega,\,n}}\int d\,x_b \int d\,x_a \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1\\ &\quad\times\psi_n^*(x_b)\,(\,x_b\,t_b \mid x_2\,t_2\,)_\omega\,V(x_2)\,(x_2\,t_2 \mid x_1\,t_1)\\ &\quad\times V(x_1)\,(\,x_1\,t_1 \mid x_a\,t_a\,)_\omega\,\psi_n(x_a)\end{aligned} \tag{3.502}$$

As in (3.481), we can write (3.497) as a cumulant expansion

$$(n\,;\,t_b,\,t_a) = Z_{\mathrm{QM},\,\omega,\,n}\,e^{i\langle n|\mathcal{A}_{\mathrm{int}}|n\rangle_\omega/\hbar}\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{i}{\hbar}\right)^m\langle n \mid \mathcal{A}_{\mathrm{int}}^m \mid n\rangle_{\omega,c} \tag{3.503}$$

where

$$\begin{aligned}\langle n \mid \mathcal{A}_{\mathrm{int}}^n \mid n\rangle_{\omega,\,c} &\equiv \langle n \mid \Delta\mathcal{A}_{\mathrm{int}}^n \mid n\rangle_\omega\\ \Delta\mathcal{A}_{\mathrm{int}} &= \mathcal{A}_{\mathrm{int}} - \langle n \mid \mathcal{A}_{\mathrm{int}} \mid n\rangle_\omega\end{aligned} \tag{3.503a}$$

For example,

$$\langle n \mid \mathcal{A}_{\mathrm{int}} \mid n\rangle_{\omega,\,c} = \left\langle n \,\middle|\, \left(\mathcal{A}_{\mathrm{int}} - \langle n \mid \mathcal{A}_{\mathrm{int}} \mid n\rangle_\omega\right) \,\middle|\, n\right\rangle_\omega = 0 \tag{3.504a}$$

$$\langle n \mid \mathcal{A}_{\text{int}}^2 \mid n \rangle_{\omega,c} = \left\langle n \,\middle|\, \left(\mathcal{A}_{\text{int}} - \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega\right)^2 \,\middle|\, n \right\rangle_\omega$$
$$= \langle n \mid \mathcal{A}_{\text{int}}^2 \mid n \rangle_\omega - \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega^2 \qquad (3.504)$$
$$\langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \rangle_{\omega,c} = \left\langle n \,\middle|\, \left(\mathcal{A}_{\text{int}} - \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega\right)^3 \,\middle|\, n \right\rangle_\omega$$
$$= \langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \rangle_\omega - 3 \langle n \mid \mathcal{A}_{\text{int}}^2 \mid n \rangle_\omega \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega \qquad (3.505)$$
$$+2 \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega^3$$

In analogy with (3.500), we can write

$$(n\,;\, t_b,\, t_a) = e^{-i\,\mathcal{E}_n\,(t_b - t_a)/\hbar}$$

where $\mathcal{E}_n$ is the energy of the n^{th} level in the presence of the perturbation V. Hence

$$\mathcal{E}_n = \lim_{t_b - t_a \to \infty} \frac{i\hbar}{t_b - t_a} \ln(n\,;\, t_b,\, t_a) \qquad (3.506a)$$

where the limit is added to ensure that no transient effect survives.

(3.503) thus gives

$$\Delta E_n = \mathcal{E}_n - E_n$$
$$= \lim_{t_b - t_a \to \infty} \frac{i\hbar}{t_b - t_a} \left\{ \frac{i}{\hbar} \langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega + \frac{1}{2!} \left(\frac{i}{\hbar}\right)^2 \langle n \mid \mathcal{A}_{\text{int}}^2 \mid n \rangle_{\omega,c} \right. \qquad (3.506)$$
$$\left. + \frac{1}{3!} \left(\frac{i}{\hbar}\right)^3 \langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \rangle_{\omega,c} + \ldots \right\}$$

which is a generalization of (3.485).

Using (3.507) [the real-time version of (3.496)], (3.501) becomes

$$\langle n \mid \mathcal{A}_{\text{int}} \mid n \rangle_\omega = -\frac{1}{Z_{\text{QM},\,\omega,\,n}} \sum_{m,\,k=0}^{\infty} \int d\,x_b \int d\,x_a \int_{t_a}^{t_b} d\,t_1 \int d\,x_1$$
$$\times\, \psi_n^*(x_b)\, \psi_m(x_b)\, \psi_m^*(x_1)\, e^{-i\,E_m\,(t_b - t_1)/\hbar}\, V(x_1)$$
$$\times\, \psi_k(x_1)\, \psi_k^*(x_a)\, e^{-i\,E_k\,(t_1 - t_a)/\hbar}\, \psi_n(x_a)$$
$$= -\frac{1}{Z_{\text{QM},\,\omega,\,n}} \sum_{m,\,k=0}^{\infty} \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\;\; \delta_{n\,m}\, \psi_m^*(x_1)\, e^{-i\,E_m\,(t_b - t_1)/\hbar}\, V(x_1)$$
$$\times\, \psi_k(x_1)\, \delta_{k\,n}\, e^{-i\,E_k\,(t_1 - t_a)/\hbar}$$
$$= -\frac{1}{Z_{\text{QM},\,\omega,\,n}} \int_{t_a}^{t_b} d\,t_1 \int d\,x_1\, \psi_n^*(x_1)\, V(x_1)\, \psi_n(x_1)\, e^{-i\,E_n\,(t_b - t_a)/\hbar}$$
$$= -\int_{t_a}^{t_b} d\,t_1 \int d\,x_1\, \psi_n^*(x_1)\, V(x_1)\, \psi_n(x_1) \quad \text{[(3.500) used.]}$$
$$= -(t_b - t_a)\, V_{n\,n} \qquad (3.508)$$

where

$$V_{n\,n} = \int d\,x_1\, \psi_n^*(x_1)\, V(x_1)\, \psi_n(x_1) \qquad (3.508a)$$

Similarly, (3.502) becomes

$$\frac{1}{2} \langle n \mid \mathcal{A}_{\text{int}}^2 \mid n \rangle_\omega = \frac{1}{Z_{\text{QM},\,\omega,\,n}} \sum_{m,\,k,\,j=0}^{\infty} \int d\,x_b \int d\,x_a \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1$$
$$\times\, \psi_n^*(x_b)\, \psi_m(x_b)\, \psi_m^*(x_2)\, e^{-i\,E_m\,(t_b - t_2)/\hbar}\, V(x_2)$$
$$\times\, \psi_k(x_2)\, \psi_k^*(x_1)\, e^{-i\,E_k\,(t_2 - t_1)/\hbar}\, V(x_1)$$
$$\times\, \psi_j(x_1)\, \psi_j^*(x_a)\, e^{-i\,E_j\,(t_1 - t_a)/\hbar}\, \psi_n(x_a)$$

$$= \frac{1}{Z_{\mathrm{QM},\omega,n}} \sum_{m,k,j=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1$$
$$\times \delta_{n\,m}\, \psi_m^*(x_2)\, e^{-i E_m (t_b - t_2)/\hbar}\, V(x_2)$$
$$\times \psi_k(x_2)\, \psi_k^*(x_1)\, e^{-i E_k (t_2 - t_1)/\hbar}\, V(x_1)$$
$$\times \psi_j(x_1)\, \delta_{j\,n}\, e^{-i E_j (t_1 - t_a)/\hbar}$$
$$= \frac{1}{Z_{\mathrm{QM},\omega,n}} \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1$$
$$\times \psi_n^*(x_2)\, e^{-i E_n (t_b - t_2)/\hbar}\, V(x_2)$$
$$\times \psi_k(x_2)\, \psi_k^*(x_1)\, e^{-i E_k (t_2 - t_1)/\hbar}\, V(x_1)$$
$$\times \psi_n(x_1)\, e^{-i E_n (t_1 - t_a)/\hbar}$$
$$= \frac{1}{Z_{\mathrm{QM},\omega,n}} \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1$$
$$\times e^{-i E_n (t_b - t_2)/\hbar}\, e^{-i E_k (t_2 - t_1)/\hbar}\, e^{-i E_n (t_1 - t_a)/\hbar}$$
$$\times \psi_n^*(x_2)\, V(x_2)\, \psi_k(x_2)\, \psi_k^*(x_1)\, V(x_1)\, \psi_n(x_1)$$
$$= \frac{1}{Z_{\mathrm{QM},\omega,n}} \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_2} d\,t_1 \tag{3.509}$$
$$\times\, e^{-i E_n (t_b - t_2)/\hbar}\, e^{-i E_k (t_2 - t_1)/\hbar}\, e^{-i E_n (t_1 - t_a)/\hbar}\, V_{n\,k}\, V_{k\,n}$$
$$= \frac{1}{Z_{\mathrm{QM},\omega,n}} \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_2} d\,t_1$$
$$\times\, e^{-i E_n (t_b - t_a)/\hbar}\, e^{i (E_n - E_k) t_2/\hbar}\, e^{-i (E_n - E_k) t_1/\hbar}\, V_{n\,k}\, V_{k\,n}$$
$$= \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_2} d\,t_1\, e^{i (E_n - E_k)(t_2 - t_1)/\hbar}\, V_{n\,k}\, V_{k\,n} \tag{3.510}$$
$$= \sum_{k=0}^{\infty} \int_{t_a}^{t_b} d\,t_2\, e^{i (E_n - E_k) t_2/\hbar} \frac{i\,\hbar}{E_n - E_k} \left[e^{-i (E_n - E_k) t_2/\hbar} - e^{-i (E_n - E_k) t_a/\hbar} \right] V_{n\,k}\, V_{k\,n}$$
$$= i\,\hbar \sum_{k=0}^{\infty} \frac{V_{n\,k}\, V_{k\,n}}{E_n - E_k} \int_{t_a}^{t_b} d\,t_2 \left[1 - e^{i (E_n - E_k)(t_2 - t_a)/\hbar} \right]$$
$$= i\,\hbar \sum_{k=0}^{\infty} \frac{V_{n\,k}\, V_{k\,n}}{E_n - E_k} \left\{ t_b - t_a + \frac{i\,\hbar}{E_n - E_k} \left[e^{i (E_n - E_k)(t_b - t_a)/\hbar} - 1 \right] \right\}$$
$$= \sum_{k=0}^{\infty} \frac{V_{n\,k}\, V_{k\,n}}{E_n - E_k} \left\{ i\,\hbar\,(t_b - t_a) - \frac{\hbar^2}{E_n - E_k} \left[e^{i (E_n - E_k)(t_b - t_a)/\hbar} - 1 \right] \right\} \tag{3.511}$$

The term $n = k$ must be treated with care. Indeed, the $n = k$ term in (3.510) gives

$$\int_{t_a}^{t_b} d\,t_2 \int_{t_a}^{t_2} d\,t_1\, V_{n\,n}^2 = V_{n\,n}^2 \int_{t_a}^{t_b} d\,t_2\, (t_2 - t_a)$$
$$= V_{n\,n}^2 \left\{ \frac{1}{2} \left(t_b^2 - t_a^2 \right) - t_a\,(t_b - t_a) \right\}$$
$$= \frac{1}{2} V_{n\,n}^2\, (t_b - t_a)^2 \tag{3.521}$$

Hence, (3.511) becomes

$$\frac{1}{2} \left\langle n \mid \mathcal{A}_{\mathrm{int}}^2 \mid n \right\rangle_\omega$$
$$= \frac{1}{2} V_{n\,n}^2\, (t_b - t_a)^2 + \sum_{k \neq n} \frac{V_{n\,k}\, V_{k\,n}}{E_n - E_k} \left\{ i\,\hbar\,(t_b - t_a) - \frac{\hbar^2}{E_n - E_k} \left[e^{i (E_n - E_k)(t_b - t_a)/\hbar} - 1 \right] \right\}$$

$$\approx \frac{1}{2} V_{nn}^2 (t_b - t_a)^2 + i\hbar (t_b - t_a) \sum_{k\neq n} \frac{V_{nk} V_{kn}}{E_n - E_k} \quad \text{for} \quad t_b - t_a \to \infty \tag{3.513}$$

Note that the same result can also be obtained by writing (3.511) as

$$\frac{1}{2}\langle n \mid \mathcal{A}_{\text{int}}^2 \mid n\rangle_\omega = \sum_{k=0}^{\infty} \frac{V_{nk} V_{kn}}{E_n - E_k + i\eta}\left\{ i\hbar (t_b - t_a) - \frac{\hbar^2}{E_n - E_k + i\eta}\left[e^{i(E_n - E_k)(t_b - t_a)/\hbar} - 1\right]\right\}$$

where $\eta = 0_+$.

The $n \neq k$ terms remain unchanged while the $n = k$ term becomes

$$\frac{V_{nn} V_{nn}}{i\eta}\left\{ i\hbar (t_b - t_a) - \frac{\hbar^2}{i\eta}\left[e^{-\eta(t_b - t_a)/\hbar} - 1\right]\right\}$$

$$\approx \frac{V_{nn} V_{nn}}{i\eta}\left\{ i\hbar (t_b - t_a) - \frac{\hbar^2}{i\eta}\left[-\frac{\eta}{\hbar}(t_b - t_a) + \frac{\eta^2}{2\hbar^2}(t_b - t_a)^2 + \ldots\right]\right\}$$

$$= \frac{1}{2} V_{nn}^2 (t_b - t_a)^2$$

in agreement with (3.521).

With the help of (3.508), (3.504) gives

$$\frac{1}{2}\langle n \mid \mathcal{A}_{\text{int}}^2 \mid n\rangle_{\omega, c} = i\hbar (t_b - t_a) \sum_{k\neq n} \frac{V_{nk} V_{kn}}{E_n - E_k} \tag{3.514}$$

The energy shift (3.506) thus becomes

$$\Delta E_n = V_{nn} + \sum_{k\neq n} \frac{V_{nk} V_{kn}}{E_n - E_k} + \ldots$$

$$\equiv \Delta_1 E_n + \Delta_2 E_n + \ldots \tag{3.515}$$

For the 3rd order perturbation, we have

$$\frac{1}{3!}\langle n \mid \mathcal{A}_{\text{int}}^3 \mid n\rangle_\omega$$

$$= -\frac{1}{Z_{\text{QM},\omega,n}} \sum_{m,k,j,i=0}^{\infty} \int d x_b \int d x_a \int_{t_a}^{t_b} d t_3 \int d x_3 \int_{t_a}^{t_3} d t_2 \int d x_2 \int_{t_a}^{t_2} d t_1 \int d x_1$$

$$\times \psi_n^*(x_b)\, \psi_m(x_b)\, \psi_m^*(x_3)\, e^{-i E_m (t_b - t_3)/\hbar}\, V(x_3)$$

$$\times \psi_k(x_3)\, \psi_k^*(x_2)\, e^{-i E_k (t_3 - t_2)/\hbar}\, V(x_2)$$

$$\times \psi_j(x_2)\, \psi_j^*(x_1)\, e^{-i E_j (t_2 - t_1)/\hbar}\, V(x_1)$$

$$\times \psi_i(x_1)\, \psi_i^*(x_a)\, e^{-i E_i (t_1 - t_a)/\hbar}\, \psi_n(x_a)$$

$$= -\frac{1}{Z_{\text{QM},\omega,n}} \sum_{m,k,j,i=0}^{\infty} \int_{t_a}^{t_b} d t_3 \int d x_3 \int_{t_a}^{t_3} d t_2 \int d x_2 \int_{t_a}^{t_2} d t_1 \int d x_1$$

$$\times \delta_{nm}\, \psi_m^*(x_3)\, e^{-i E_m (t_b - t_3)/\hbar}\, V(x_3)$$

$$\times \psi_k(x_3)\, \psi_k^*(x_2)\, e^{-i E_k (t_3 - t_2)/\hbar}\, V(x_2)$$

$$\times \psi_j(x_2)\, \psi_j^*(x_1)\, e^{-i E_j (t_2 - t_1)/\hbar}\, V(x_1)$$

$$\times \psi_i(x_1)\, \delta_{in}\, e^{-i E_i (t_1 - t_a)/\hbar}$$

$$= -\frac{1}{Z_{\text{QM},\omega,n}} \sum_{k,j=0}^{\infty} \int_{t_a}^{t_b} d t_3 \int d x_3 \int_{t_a}^{t_3} d t_2 \int d x_2 \int_{t_a}^{t_2} d t_1 \int d x_1$$

$$\times \psi_n^*(x_3)\, e^{-i E_n (t_b - t_3)/\hbar}\, V(x_3)$$

$$\times \psi_k(x_3)\, \psi_k^*(x_2)\, e^{-i E_k (t_3 - t_2)/\hbar}\, V(x_2)$$

$$\times \psi_j(x_2)\, \psi_j^*(x_1)\, e^{-i E_j (t_2 - t_1)/\hbar}\, V(x_1)$$

$$\times \psi_n(x_1)\, e^{-i E_n (t_1 - t_a)/\hbar}$$

$$= -\frac{1}{Z_{\mathrm{QM},\,\omega,\,n}} \sum_{k,j=0}^{\infty} \int_{t_a}^{t_b} d\,t_3 \int d\,x_3 \int_{t_a}^{t_3} d\,t_2 \int d\,x_2 \int_{t_a}^{t_2} d\,t_1 \int d\,x_1$$

$$\times e^{-i E_n (t_b - t_3)/\hbar}\, e^{-i E_k (t_3 - t_2)/\hbar}\, e^{-i E_j (t_2 - t_1)/\hbar}\, e^{-i E_n (t_1 - t_a)/\hbar}$$

$$\times \psi_n^*(x_3)\, V(x_3)\, \psi_k(x_3)\, \psi_k^*(x_2)\, V(x_2)\, \psi_j(x_2)\, \psi_j^*(x_1)\, V(x_1)\, \psi_n(x_1)$$

$$= -\sum_{k,j=0}^{\infty} \int_{t_a}^{t_b} d\,t_3 \int_{t_a}^{t_3} d\,t_2 \int_{t_a}^{t_2} d\,t_1 \qquad (3.515a)$$

$$\times e^{i (E_n - E_k)\, t_3/\hbar}\, e^{i (E_k - E_j)\, t_2/\hbar}\, e^{i (E_j - E_n)\, t_1/\hbar}\, V_{n k}\, V_{k j}\, V_{j n}$$

The time integrals are evaluated using *Mathematica* [see "3.18._Code.nb"] to give

$$\frac{1}{3!}\langle n \mid \mathcal{A}_{\mathrm{int}}^3 \mid n\rangle_\omega = \sum_{k,j=0}^{\infty} V_{n k}\, V_{k j}\, V_{j n} \left\{ \frac{\hbar^2 (t_b - t_a)}{(E_n - E_k)(E_n - E_j)} \right. \qquad (3.515b)$$

$$- \frac{i \hbar^3}{E_k - E_j} \left[\frac{1}{(E_n - E_k)^2} \left(1 - e^{i (E_n - E_k)(t_b - t_a)/\hbar}\right) \right.$$

$$\left. \left. - \frac{1}{(E_n - E_j)^2} \left(1 - e^{i (E_n - E_j)(t_b - t_a)/\hbar}\right) \right] \right\}$$

As before, for k, $j \neq n$, the 2nd term in the curly bracket can be ignored as $t_b - t_a \to \infty$.

For $k = n \neq j$, we use the $i\,\eta$ trick to get

$$V_{n n}\, V_{n j}\, V_{j n} \left\{ \frac{\hbar^2 (t_b - t_a)}{i\,\eta\,(E_n - E_j)} - \frac{i \hbar^3}{E_n - E_j} \frac{1}{(i\,\eta)^2} \left(1 - e^{-\eta (t_b - t_a)/\hbar}\right) \right\}$$

$$\approx V_{n n}\, V_{n j}\, V_{j n} \frac{i \hbar^3}{E_n - E_j} \frac{1}{(i\,\eta)^2} \frac{1}{2} \left[\frac{\eta}{\hbar} (t_b - t_a) \right]^2$$

$$= -\frac{1}{2} V_{n n}\, V_{n j}\, V_{j n} \frac{i \hbar}{E_n - E_j} (t_b - t_a)^2 \qquad (3.515c)$$

For $j = n \neq k$, the $i\,\eta$ trick gives

$$V_{n k}\, V_{k n}\, V_{n n} \left\{ \frac{\hbar^2 (t_b - t_a)}{(E_n - E_k)\, i\,\eta} + \frac{i \hbar^3}{E_k - E_n} \frac{1}{(i\,\eta)^2} \left(1 - e^{-\eta (t_b - t_a)/\hbar}\right) \right\}$$

$$\approx V_{n k}\, V_{k n}\, V_{n n} \frac{i \hbar^3}{E_k - E_n} \frac{1}{(i\,\eta)^2} \left(-\frac{1}{2}\right) \left[\frac{\eta}{\hbar} (t_b - t_a) \right]^2$$

$$= -\frac{1}{2} V_{n k}\, V_{k n}\, V_{n n} \frac{i \hbar}{E_n - E_k} (t_b - t_a)^2 \qquad (3.515d)$$

For $j = n = k$, (3.515a) gives [see "3.18._Code.nb"]

$$-\int_{t_a}^{t_b} d\,t_3 \int_{t_a}^{t_3} d\,t_2 \int_{t_a}^{t_2} d\,t_1\, V_{n n}^3 = -\frac{1}{6} (t_b - t_a)^3\, V_{n n}^3 \qquad (3.515e)$$

Since (3.515c) & (3.515d) give the same contribution after the sum, (3.515b) becomes, for $t_b - t_a \to \infty$,

$$\frac{1}{3!}\langle n \mid \mathcal{A}_{\mathrm{int}}^3 \mid n\rangle_\omega = \sum_{k \neq n,\, j \neq n} V_{n k}\, V_{k j}\, V_{j n} \frac{\hbar^2 (t_b - t_a)}{(E_n - E_k)(E_n - E_j)}$$

$$- \sum_{k \neq n} V_{n k}\, V_{k n}\, V_{n n} \frac{i \hbar}{E_n - E_k} (t_b - t_a)^2 - \frac{1}{6} (t_b - t_a)^3\, V_{n n}^3$$

$$\rightarrow \quad \frac{1}{3!}\left\langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \right\rangle_{\omega,c} = \frac{1}{3!}\Big\{ \left\langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \right\rangle_{\omega} + 3\left[V_{nn}^2 (t_b - t_a)^2 + 2 i \hbar (t_b - t_a) \sum_{k \neq n} \frac{V_{nk} V_{kn}}{E_n - E_k} \right] (t_b - t_a) V_{nn} - 2\left[(t_b - t_a) V_{nn} \right]^3 \Big\}$$

$$= \sum_{k \neq n, j \neq n} V_{nk} V_{kj} V_{jn} \frac{\hbar^2 (t_b - t_a)}{(E_n - E_k)(E_n - E_j)}$$

$$\therefore \quad \Delta_3 E_n = \lim_{t_b - t_a \to \infty} \frac{i\hbar}{t_b - t_a} \frac{1}{3!} \left(\frac{i}{\hbar}\right)^3 \left\langle n \mid \mathcal{A}_{\text{int}}^3 \mid n \right\rangle_{\omega,c}$$

$$= \sum_{k \neq n, j \neq n} \frac{V_{nk} V_{kj} V_{jn}}{(E_n - E_k)(E_n - E_j)} \qquad (3.516a)$$

which differs from Kleinert's (3.516) considerably.

For comparison, we recall the Brillouin-Wigner eq. for energy shift

$$\Delta E_n = \mathcal{E}_n - E_n = \overline{R}_{nn}(E_n + \Delta E_n) = \overline{R}_{nn}(\mathcal{E}_n) \qquad (3.517)$$

where $\mathcal{E}_n$ is the exact energy of level n and

$$\overline{R}_{nn} = \langle n \mid \hat{\overline{R}} \mid n \rangle$$

and $\hat{\overline{R}}$ satisfies

$$\hat{\overline{R}}(E) = \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{\overline{R}}(E) \qquad (3.518)$$

with

$$\hat{P}_n = \mid n \rangle \langle n \mid \qquad (3.518a)$$

being the projection operator onto the state $\mid n \rangle$.

Solving (3.518) by iteration, we have

$$\hat{\overline{R}}(E) = \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \left[\hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{\overline{R}}(E) \right]$$

$$= \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{\overline{R}}(E)$$

$$= \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} + \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} \qquad (3.519)$$

$$+ \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{V} \frac{1 - \hat{P}_n}{E - \hat{H}_\omega} \hat{\overline{R}}(E)$$

Setting $\mathcal{E}_n = E$ in (3.517) a d using (3.519) then gives

$$E - E_n = R_{nn}(E) = \langle n \mid \hat{\overline{R}}(E) \mid n \rangle$$

$$= V_{nn} + \sum_{k \neq n} \frac{V_{nk} V_{kn}}{E - E_k} + \sum_{k, j \neq n} \frac{V_{nk} V_{kj} V_{jn}}{(E - E_k)(E - E_j)} + ... \qquad (3.520)$$

which is simply the cumulant expansion (3.506) with E_n replaced by E.

(3.517) can be Taylor expanded as

$$\Delta E_n \approx \sum_{k=0}^{\infty} \frac{(\Delta E_n)^k}{k!} \overline{R}_{nn}^{(k)}(E_n) \qquad (3.521a)$$

where

$$\overline{R}^{(k)}_{n\,n}(E_n) = \left.\frac{d^k\,\overline{R}_{n\,n}(E)}{d\,E^k}\right|_{E=E_n} \tag{3.521b}$$

Chopping off the sum at $k = N$, we have

$$\Delta^{[N]}\,E_n = \sum_{k=0}^{N} \Delta_k\,E_n \;=\sum_{k=0}^{N} \frac{(\Delta\,E_n)^k}{k!}\,\overline{R}^{(k)}_{n\,n}(E_n) \tag{3.521c}$$

which can be solved iteratively if we approximate it with

$$\Delta^{[N]}\,E_n = R_{n\,n}(E_n) + \sum_{k=1}^{N} \frac{\left(\Delta^{[N-k]}\,E_n\right)^k}{k!}\,\overline{R}^{(k)}_{n\,n}(E_n) \tag{3.521d}$$

Starting with $N = 0$, we have

$$\Delta^{[0]}\,E_n = \Delta_0\,E_n = R_{n\,n}(E_n) \tag{3.521e}$$

For $N = 1$,

$$\Delta^{[1]}\,E_n = \Delta_0\,E_n + \Delta_1\,E_n$$
$$= R_{n\,n}\,(E_n) + \Delta^{[0]}\,E_n\,\overline{R}'_{n\,n}(E_n)$$

Using (3.521e), we have

$$\Delta_1\,E_n = \Delta^{[0]}\,E_n\,\overline{R}'_{n\,n}(E_n)$$
$$= R_{n\,n}(E_n)\,\overline{R}'_{n\,n}(E_n) \tag{3.521f}$$

For $N = 2$,

$$\Delta^{[2]}\,E_n = \Delta_0\,E_n + \Delta_1\,E_n + \Delta_2\,E_n$$
$$= R_{n\,n}\,(E_n) + \Delta^{[1]}\,E_n\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2!}\left(\Delta^{[0]}\,E_n\right)^2\overline{R}''_{n\,n}(E_n)$$
$$= R_{n\,n}\,(E_n) + (\Delta_0\,E_n + \Delta_1\,E_n)\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2}\,(\Delta_0\,E_n)^2\,\overline{R}''_{n\,n}(E_n)$$

Using (3.521e-f), we have

$$\Delta_2\,E_n = \Delta_1\,E_n\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2}\,(\Delta_0\,E_n)^2\,\overline{R}''_{n\,n}(E_n)$$
$$= R_{n\,n}(E_n)\,\overline{R}'^{\,2}_{n\,n}(E_n) + \frac{1}{2}\,R^2_{n\,n}(E_n)\,\overline{R}''_{n\,n}(E_n) \tag{3.521g}$$

For $N = 3$,

$$\Delta^{[3]}\,E_n = \Delta_0\,E_n + \Delta_1\,E_n + \Delta_2\,E_n + \Delta_3\,E_n$$
$$= R_{n\,n}\,(E_n) + \Delta^{[2]}\,E_n\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2}\left(\Delta^{[1]}\,E_n\right)^2\overline{R}''_{n\,n}(E_n) + \frac{1}{3!}\left(\Delta^{[0]}\,E_n\right)^3\overline{R}'''_{n\,n}(E_n)$$
$$= R_{n\,n}\,(E_n) + (\Delta_0\,E_n + \Delta_1\,E_n + \Delta_2\,E_n)\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2}\,(\Delta_0\,E_n + \Delta_1\,E_n)^2\,\overline{R}''_{n\,n}(E_n)$$
$$+\frac{1}{3!}\left(\Delta^{[0]}\,E_n\right)^3\overline{R}'''_{n\,n}(E_n)$$

Using (3.521e-g), we have

$$\Delta_3\,E_n = \Delta_2\,E_n\,\overline{R}'_{n\,n}(E_n) + \frac{1}{2}\left[2\,\Delta_0\,E_n\,\Delta_1\,E_n + (\Delta_1\,E_n)^2\right]\overline{R}''_{n\,n}(E_n) + \frac{1}{3!}\left(\Delta^{[0]}\,E_n\right)^3\overline{R}'''_{n\,n}(E_n)$$
$$= R_{n\,n}(E_n)\,\overline{R}'^{\,3}_{n\,n}(E_n) + \frac{3}{2}\,R^2_{n\,n}(E_n)\,\overline{R}'_{n\,n}(E_n)\,\overline{R}''_{n\,n}(E_n) \tag{3.521h}$$
$$+\frac{1}{2}\,R^2_{n\,n}(E_n)\,\overline{R}'^{\,2}_{n\,n}(E_n)\,\overline{R}''_{n\,n}(E_n) + \frac{1}{3!}\,R^3_{n\,n}(E_n)\,\overline{R}'''_{n\,n}(E_n)$$

Combining (3.521e-h), we have

$$\begin{aligned}\Delta^{[3]} E_n = {} & R_{nn}(E_n) + R_{nn}(E_n)\,\overline{R}'_{nn}(E_n) \\ & + R_{nn}(E_n)\,\overline{R}'^{2}_{nn}(E_n) + \frac{1}{2} R^2_{nn}(E_n)\,\overline{R}''_{nn}(E_n) \\ & + R_{nn}(E_n)\,\overline{R}'^{3}_{nn}(E_n) + \frac{3}{2} R^2_{nn}(E_n)\,\overline{R}'_{nn}(E_n)\,\overline{R}''_{nn}(E_n) \\ & + \frac{1}{2} R^2_{nn}(E_n)\,\overline{R}'^{2}_{nn}(E_n)\,\overline{R}''_{nn}(E_n) + \frac{1}{3!} R^3_{nn}(E_n)\,\overline{R}'''_{nn}(E_n)\end{aligned} \qquad (3.521)$$

Since the values of the $\Delta_k E_n$'s remain the same for all orders of iteration, we can calculate it directly. Subtracting

$$\Delta^{[N-1]} E_n = R_{nn}(E_n) + \sum_{k=1}^{N-1} \frac{\left(\Delta^{[N-k-1]} E_n\right)^k}{k!} \overline{R}^{(k)}_{nn}(E_n)$$

from (3.521d), we get the iteration formula

$$\begin{aligned}\Delta_N E_n &= \frac{(\Delta_0 E_n)^N}{N!} \overline{R}^{(N)}_{nn}(E_n) + \sum_{k=1}^{N-1} \frac{\left(\Delta^{[N-k]} E_n\right)^k - \left(\Delta^{[N-k-1]} E_n\right)^k}{k!} \overline{R}^{(k)}_{nn}(E_n) \\ &= \frac{(\Delta_0 E_n)^N}{N!} \overline{R}^{(N)}_{nn}(E_n) + \sum_{k=1}^{N-1} \frac{\left(\sum_{j=0}^{N-k} \Delta_j E_n\right)^k - \left(\sum_{j=0}^{N-k-1} \Delta_j E_n\right)^k}{k!} \overline{R}^{(k)}_{nn}(E_n)\end{aligned} \qquad (3.521j)$$

Energy shifts for $V(x) = \frac{1}{4} g x^4$ are calculated in Appendix 3B [see "A3B._Code.nb"], which gives

$$\begin{aligned}\Delta E_n = {} & \frac{1}{4} g\left(3 + 6n + 6n^2\right)\gamma^4 - \frac{g^2\left(21 + 59n + 51n^2 + 34n^3\right)\gamma^8}{16\,\omega} \\ & + \frac{g^3\left(111 + 347n + 472n^2 + 250n^3 + 125n^4\right)\gamma^{12}}{32\,\omega^2} + O\left[g^4\right]\end{aligned} \qquad (3.522)$$

where

$$\gamma = \sqrt{\frac{\hbar}{2 M \omega}}$$