

8-5. A transition element which employs the same wave function as both the initial and final states is called an expectation value. Thus the expectation value of F for the ground state Φ_0 of equation (8.83) is

$$\langle \Phi_0 | F | \Phi_0 \rangle = \int \cdots \int \Phi_0^* F \Phi_0 dQ_1 dQ_2 \cdots dQ_{N-1} \quad (8.84)$$

(The integral over complex variables is defined as equal to the corresponding integral over real normal coordinates Q_α^c and Q_α^s .) Show that the following expectation values are correct (for $\alpha \neq 0$).

$$\begin{aligned} \langle \Phi_0^* | Q_\alpha | \Phi_0 \rangle &= \langle \Phi_0^* | Q_\alpha^* | \Phi_0 \rangle = 0 \\ \langle \Phi_0^* | Q_\alpha^2 | \Phi_0 \rangle &= \langle \Phi_0^* | Q_\alpha^{*2} | \Phi_0 \rangle = 0 \\ \langle \Phi_0^* | Q_\alpha^* Q_\alpha | \Phi_0 \rangle &= \frac{\hbar}{2\omega_\alpha} \langle \Phi_0^* | 1 | \Phi_0 \rangle \\ \langle \Phi_0^* | Q_\alpha^* Q_\alpha | \Phi_0 \rangle &= 0, \quad \alpha \neq \beta \end{aligned} \quad (8.85)$$

Recall that

$$Q_\alpha = \frac{1}{\sqrt{2}}(Q_\alpha^c - iQ_\alpha^s)$$

Hence

$$Q_\alpha^* Q_\alpha = \frac{1}{2}(Q_\alpha^c)^2 + \frac{1}{2}(Q_\alpha^s)^2 \quad (1)$$

Consider equation (8.83).

$$\Phi_0 = A \exp \left(-\frac{1}{2\hbar} \sum_{\alpha=1}^{N-1} \omega_\alpha Q_\alpha^* Q_\alpha \right) \quad (8.83)$$

It follows that

$$\Phi_0^* \Phi_0 = A^2 \exp \left(-\frac{1}{\hbar} \sum_{\alpha=1}^{N-1} \omega_\alpha Q_\alpha^* Q_\alpha \right) \quad (2)$$

Substitute (1) into (2).

$$\Phi_0^* \Phi_0 = A^2 \exp \left(-\frac{1}{2\hbar} \sum_{\alpha=1}^{N-1} \omega_\alpha ((Q_\alpha^c)^2 + (Q_\alpha^s)^2) \right)$$

For brevity in the following formulas, let

$$u = \Psi_0^* \Psi_0$$

We will use the following integrals.

$$\int_{-\infty}^{\infty} \exp(-ax^2 + b) dx = \sqrt{\frac{\pi}{a}} \exp(b) \quad (1)$$

$$\int_{-\infty}^{\infty} x \exp(-ax^2 + b) dx = 0 \quad (2)$$

$$\int_{-\infty}^{\infty} x^2 \exp(-ax^2 + b) dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}} \exp(b) \quad (3)$$

Here are some specific examples with $a = \omega_1/2\hbar$.

$$\int_{-\infty}^{\infty} u dQ_1^c = \left(\frac{2\pi\hbar}{\omega_1} \right)^{1/2} u \exp \left(\frac{\omega_1}{2\hbar} (Q_1^c)^2 \right) \quad (4)$$

$$\int_{-\infty}^{\infty} Q_1^c u dQ_1^c = 0 \quad (5)$$

$$\int_{-\infty}^{\infty} (Q_1^c)^2 u dQ_1^c = \frac{\hbar}{\omega_1} \left(\frac{2\pi\hbar}{\omega_1} \right)^{1/2} u \exp \left(\frac{\omega_1}{2\hbar} (Q_1^c)^2 \right) \quad (6)$$

Note that multiplying u by an exponential cancels a factor, i.e.,

$$\exp(b) = u \exp \left(\frac{\omega_1}{2\hbar} (Q_1^c)^2 \right)$$

Compute the expectation value for Q_1 . Let

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u \frac{Q_1^c - iQ_1^s}{\sqrt{2}} dQ_1^c dQ_1^s$$

By equation (2), $I = 0$ hence by equation (8.84)

$$\langle \Phi_0^* | Q_1 | \Phi_0 \rangle = 0$$

Compute the expectation value for Q_1^* . Let

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u \frac{Q_1^c + iQ_1^s}{\sqrt{2}} dQ_1^c dQ_1^s$$

As above, $I = 0$ hence

$$\langle \Phi_0^* | Q_1^* | \Phi_0 \rangle = 0$$

Compute the expectation value for Q_1^2 . Let

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u \left(\frac{Q_1^c - iQ_1^s}{\sqrt{2}} \right)^2 dQ_1^c dQ_1^s$$

Rewrite as

$$\begin{aligned} I &= -i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u Q_1^c Q_1^s dQ_1^c dQ_1^s \\ &\quad + \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (Q_1^c)^2 dQ_1^c dQ_1^s - \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (Q_1^s)^2 dQ_1^c dQ_1^s \end{aligned}$$

The first integral vanishes by (2). The remaining integrals cancel hence

$$\langle \Phi_0^* | Q_1^2 | \Phi_0 \rangle = 0$$

Compute the expectation value for Q_1^{*2} . (As above except for a sign change.)

$$\begin{aligned} I &= i \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u Q_1^c Q_1^s dQ_1^c dQ_1^s \\ &\quad + \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (Q_1^c)^2 dQ_1^c dQ_1^s - \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (Q_1^s)^2 dQ_1^c dQ_1^s \end{aligned}$$

By the same arguments as Q_1^2

$$\langle \Phi_0^* | Q_1^{*2} | \Phi_0 \rangle = 0$$

Compute the expectation value for $Q_1^* Q_1$. Let

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u \frac{(Q_1^c)^2 + (Q_1^s)^2}{2} dQ_1^c dQ_1^s$$

Rewrite as

$$I = \frac{1}{2} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} u (Q_1^c)^2 dQ_1^c \right) dQ_1^s + \frac{1}{2} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} u (Q_1^s)^2 dQ_1^s \right) dQ_1^c$$

By equations (3) and (6)

$$\begin{aligned} I &= \frac{\hbar}{2\omega_1} \left(\frac{2\pi\hbar}{\omega_1} \right)^{1/2} \exp \left(\frac{\omega_1}{2\hbar} (Q_1^c)^2 \right) \int_{-\infty}^{\infty} u dQ_1^s \\ &\quad + \frac{\hbar}{2\omega_1} \left(\frac{2\pi\hbar}{\omega_1} \right)^{1/2} \exp \left(\frac{\omega_1}{2\hbar} (Q_1^s)^2 \right) \int_{-\infty}^{\infty} u dQ_1^c \end{aligned}$$

By equations (1) and (4)

$$I = \frac{\hbar}{2\omega_1} \frac{2\pi\hbar}{\omega_1} \exp\left(\frac{\omega_1}{2\hbar}(Q_1^c)^2\right) \exp\left(\frac{\omega_1}{2\hbar}(Q_1^s)^2\right) u \\ + \frac{\hbar}{2\omega_1} \frac{2\pi\hbar}{\omega_1} \exp\left(\frac{\omega_1}{2\hbar}(Q_1^s)^2\right) \exp\left(\frac{\omega_1}{2\hbar}(Q_1^c)^2\right) u$$

Integrate over the remaining measure as in (8.84).

$$\langle \Phi_0^* | Q_1^* Q_1 | \Phi_0 \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} I dQ_2^c dQ_2^s \cdots dQ_{N-1}^c dQ_{N-1}^s \\ = \frac{\hbar}{\omega_1} \frac{2\pi\hbar}{\omega_1} \prod_{k=2}^{N-1} \frac{2\pi\hbar}{\omega_k} \quad (7)$$

Note that the exponentials cancel with u .

Compute the normalization constant. By equations (1) and (4)

$$\langle \Phi_0^* | 1 | \Phi_0 \rangle = \prod_{k=1}^{N-1} \frac{2\pi\hbar}{\omega_k} \quad (8)$$

Hence by (7) and (8)

$$\langle \Phi_0^* | Q_1^* Q_1 | \Phi_0 \rangle = \frac{\hbar}{\omega_1} \langle \Phi_0^* | 1 | \Phi_0 \rangle$$

Compute the expectation value for $Q_1^* Q_2$. Let

$$I = \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (Q_1^c Q_2^c - Q_1^s Q_2^s - i Q_1^c Q_2^s - i Q_1^s Q_2^c) dQ_1^c dQ_1^s$$

By equation (2), $I = 0$ hence by equation (8.84)

$$\langle \Phi_0^* | Q_1^* Q_2 | \Phi_0 \rangle = 0$$

FIXME: Result should be $\hbar/2\omega_1$ instead of \hbar/ω_1 .