Going after the **Raman tensor**

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CINA

From $\boxed{24\text{Aug}12}$ p. 8, we need the Raman tensor element

$$\alpha_{10}(Q) = \sum_{n_e} \frac{\langle 1_g(Q)|n_e(Q)\rangle\langle n_e(Q)|0_g(Q)\rangle}{\epsilon_{n_e}(Q) - \epsilon_{0_g}(Q) - \Omega_1}$$

Here, $h_g(Q)|n_g(Q)\rangle = \hbar\epsilon_{n_g}(Q)|n_g(Q)\rangle$

and $h_e(Q)|n_e(Q)\rangle = \hbar\epsilon_{n_e}(Q)|n_e(Q)\rangle$,

where ($\boxed{31\text{Aug}12}$)

$$h_g(Q) = \frac{p^2}{2m} + \frac{m\omega^2(Q)}{2}(q - q_g(Q))^2 + Z(Q)$$

and

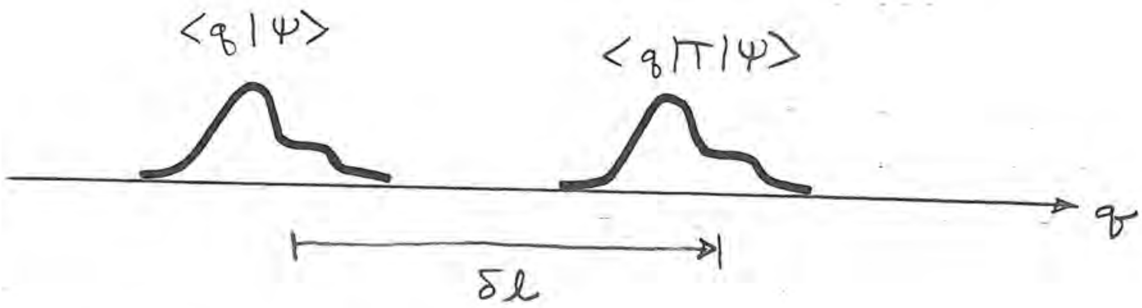
$$h_e(Q) = \frac{p^2}{2m} + \frac{m\omega^2(Q)}{2}(q - q_e(Q))^2 + Z(Q) + \hbar\epsilon \quad .$$

$q_e(Q) = q_g(Q) + \delta l$

$$\hbar\epsilon_{n_g}(Q) = \hbar\omega(Q)(n_g + \tfrac{1}{2}) + Z(Q) \quad ;$$

$$\hbar\epsilon_{n_e}(Q) = \hbar\omega(Q)(n_e + \tfrac{1}{2}) + Z(Q) + \hbar\epsilon \quad .$$

The eigenkets of $h_e(Q)$ can be related to those of $h_g(Q)$ using a vibrational spatial **translation operator** $T(\delta\ell)$ such that $\langle q|T|\psi\rangle = \langle q-\delta\ell|\psi\rangle$.



Using a series expansion,

$$\langle q|T|\psi\rangle = \sum_{m=0}^{\infty} \frac{(-\delta\ell)^m}{m!} \left(\frac{d}{dq}\right)^m \langle q|\psi\rangle$$

$$= \sum_m \frac{(-i\delta\ell/\hbar)^m}{m!} \left(\frac{\hbar}{i}\frac{d}{dq}\right)^m \langle q|\psi\rangle$$

$$= \sum_m \frac{(-i\delta\ell/\hbar)^m}{m!} \langle q|\,\hat{p}^m|\psi\rangle$$

$$= \langle q|\, e^{-i\delta\ell\hat{p}/\hbar}\,|\psi\rangle .$$

Hence,

$$\boxed{\mathbf{T(\delta\ell)} = e^{-i\delta\ell p/\hbar}}$$

and, in particular,

$$\boxed{|\mathbf{n_e(Q)}\rangle = e^{-i\delta\ell p/\hbar}\,|n_g(Q)\rangle}$$

with $n_g = n_e$.

Introducing harmonic oscillator creation and annihilation operators appropriate to

$h_g(Q) = \hbar\omega(Q)\left(a^+(Q)\,a(Q) + \frac{1}{2}\right) + Z(Q)$, we have

$q - q_g(Q) = \sqrt{\frac{\hbar}{2m\omega(Q)}}\left(a^+(Q) + a(Q)\right)$ and

$p = i\sqrt{\frac{\hbar m\omega(Q)}{2}}\left(a^+(Q) - a(Q)\right)$.

Hence,

$n_g = n_e$

$$\langle n_e(Q)|\,0_g(Q)\rangle = \langle n_g(Q)|\, e^{i\delta\ell\, p/\hbar}\,|0_g(Q)\rangle$$

$$= \langle n_g(Q)|\, e^{-\delta\ell\sqrt{\frac{m\omega(Q)}{2\hbar}}\left(a^+(Q) - a(Q)\right)}\,|0_g(Q)\rangle$$

$$= \langle n|\, e^{-\delta\ell\sqrt{\frac{m\omega}{2\hbar}}\,a^+}\, e^{\delta\ell\sqrt{\frac{m\omega}{2\hbar}}\,a}\, e^{\delta\ell^2\frac{m\omega}{4\hbar}[a^+,a]}\,|0\rangle$$

$$= e^{-\delta\ell^2\frac{m\omega}{4\hbar}}\,\langle n|\, e^{-\delta\ell\sqrt{\frac{m\omega}{2\hbar}}\,a^+}\,|0\rangle$$

$$= e^{-\delta\ell^2\frac{m\omega}{4\hbar}}\left(-\delta\ell\sqrt{\frac{m\omega}{2\hbar}}\right)^n \frac{1}{n!}\,\overbrace{\langle n|(a^+)^n|0\rangle}^{\sqrt{n!}} .$$

$$\boxed{\langle n_e(Q)|\,0_g(Q)\rangle = e^{-\delta\ell^2\frac{m\omega(Q)}{4\hbar}}\left(-\delta\ell\sqrt{\frac{m\omega(Q)}{2\hbar}}\right)^{n_e}\frac{1}{\sqrt{n_e!}}} .$$

OK, repeats; survives direct check for $n_e = 0$ (p. ②).

We also need

$$\langle 1_g(Q) | n_e(Q) \rangle = \langle 1_g(Q) | \, e^{-i\delta\ell \, p/\hbar} \, | n_g(Q) \rangle$$

$$= \langle 1_g(Q) | \, e^{\delta\ell \sqrt{\frac{m\omega(Q)}{2\hbar}} \left(a^{\dagger}(Q) - a(Q) \right)} \, | n_g(Q) \rangle$$

$$= e^{-\delta\ell^2 \frac{m\omega}{4\hbar}} \langle 1 | \, e^{\delta\ell \sqrt{\frac{m\omega}{2\hbar}} a^{\dagger}} \, e^{-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} a} \, | n \rangle$$

$$= e^{-\delta\ell^2 \frac{m\omega}{4\hbar}} \left\{ \langle 1 | + \delta\ell \sqrt{\frac{m\omega}{2\hbar}} \langle 0 | \right\} \sum_{r=0}^{n} \frac{1}{r!} \left(-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} \right)^{r} \underbrace{a^{r} | n \rangle}_{\sqrt{\frac{n!}{(n-r)!}} \, | n-r \rangle}$$

$$= e^{-\delta\ell^2 \frac{m\omega}{4\hbar}} \sum_{r=0}^{n} \frac{1}{r!} \sqrt{\frac{n!}{(n-r)!}} \left(-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} \right)^{r} \left\{ \underbrace{\langle 1 | n-r \rangle}_{\delta_{r,n-1}} + \delta\ell \sqrt{\frac{m\omega}{2\hbar}} \underbrace{\langle 0 | n-r \rangle}_{\delta_{r,n}} \right\}$$

$$= e^{-\delta\ell^2 \frac{m\omega}{4\hbar}} \left\{ \frac{\sqrt{n!}}{(n-1)!} \left(-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} \right)^{n-1} (1 - \delta_{n0}) - \frac{1}{\sqrt{n!}} \left(-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} \right)^{n+1} \right\}$$

$$= e^{-\delta\ell^2 \frac{m\omega}{4\hbar}} \frac{1}{\sqrt{n!}} \left(-\delta\ell \sqrt{\frac{m\omega}{2\hbar}} \right)^{n-1} \left\{ \overbrace{n(1 - \delta_{n0})}^{n} - \delta\ell^2 \frac{m\omega}{2\hbar} \right\}$$

$$\boxed{\langle 1_g(Q) | n_e(Q) \rangle = e^{-\delta\ell^2 \frac{m\omega(Q)}{4\hbar}} \frac{1}{\sqrt{n_e!}} \left(-\delta\ell \sqrt{\frac{m\omega(Q)}{2\hbar}} \right)^{n_e - 1} \left(n_e - \delta\ell^2 \frac{m\omega(Q)}{2\hbar} \right)}$$

OK, repeats

Substituting on p. 1, we arrive at

$$\alpha_{10}(Q) = \sum_{n_e} (\epsilon + n_e \omega(Q) - \Omega_1)^{-1} \, e^{-\delta\ell^2 \frac{m\omega(Q)}{2\hbar}} \frac{1}{n_e!} \left(-\delta\ell \sqrt{\frac{m\omega(Q)}{2\hbar}}\right)^{2n_e - 1} \left(n_e - \delta\ell^2 \frac{m\omega(Q)}{2\hbar}\right)$$

OK, repeats

$$\boxed{\alpha_{10}(Q) = -\frac{1}{\delta\ell}\sqrt{\frac{2\hbar}{m\omega(Q)}} \, e^{-\delta\ell^2 \frac{m\omega(Q)}{2\hbar}} \times \sum_{n_e=0}^{\infty} (\epsilon + n_e\omega(Q) - \Omega_1)^{-1} \left(\delta\ell^2 \frac{m\omega(Q)}{2\hbar}\right)^{n_e} \frac{1}{n_e!} \left(n_e - \delta\ell^2 \frac{m\omega(Q)}{2\hbar}\right)}$$

(a)

$$\langle n_e | 0_g \rangle = \sqrt{\frac{m\omega}{\pi\hbar}} \int_{-\infty}^{\infty} dq \, e^{-\frac{m\omega}{2\hbar}(q-\delta\ell)^2} \, e^{-\frac{m\omega}{2\hbar} q^2}$$

$$-\frac{m\omega}{2\hbar}\left(2q^2 - 2q\delta\ell + \delta\ell^2\right) = -\frac{m\omega}{\hbar}\left(q^2 - q\delta\ell\right) - \frac{m\omega}{2\hbar}\delta\ell^2$$

$$= -\frac{m\omega}{\hbar}\left[\left(q - \frac{\delta\ell}{2}\right)^2 - \frac{\delta\ell^2}{4}\right] - \frac{m\omega}{2\hbar}\delta\ell^2$$

$$= -\frac{m\omega}{\hbar}\left(q - \delta\ell/2\right)^2 - \frac{m\omega}{4\hbar}\delta\ell^2$$

$$= e^{-\frac{m\omega}{4\hbar}\delta\ell^2} \sqrt{\frac{m\omega}{\pi\hbar}} \int dq \, e^{-\frac{m\omega}{\hbar}(q - \delta\ell/2)^2} = e^{-\frac{m\omega}{2\hbar}\delta\ell^2}.$$

$\boxed{\text{agrees w/ general formula on p. (3)}}$