CHEMISTRY 273

POSITION AND MOMENTUM TRANSITION MOMENTS

Here we show the equivalence of the position and momentum transition moments:

$$\boxed{i\,\omega_{\alpha\beta}\mu\left\langle \psi^{o}_{\alpha}|\hat{x}|\psi^{o}_{\beta}\right\rangle = \left\langle \psi^{o}_{\alpha}|\hat{p}_{x}|\psi^{o}_{\beta}\right\rangle}$$

$$\omega_{\alpha\beta} = \frac{E_{\alpha} - E_{\beta}}{\hbar} \qquad \mu = \text{reduced mass}$$

where $\Psi^{o}_{k} = \psi^{o}_{k}e^{-iE^{o}_{k}t/\hbar}$ are the zeroth order solutions to the unperturbed Schrödinger equation, and thus:

(1) $\hat{H}^{o}\Psi^{o}_{k} = i\hbar\dfrac{\partial\Psi^{o}_{k}}{\partial t}$ and (1′) $\hat{H}^{o*}\Psi^{o*}_{k} = -i\hbar\dfrac{\partial\Psi^{o*}_{k}}{\partial t}$

LEMMA: $$\frac{d}{dt}\left\langle \Psi^{o}_{\alpha}|\hat{x}|\Psi^{o}_{\beta}\right\rangle = \frac{1}{\mu}\left\langle \Psi^{o}_{\alpha}|\hat{p}_{x}|\Psi^{o}_{\beta}\right\rangle$$

To prove the lemma:

$$\frac{d}{dt}\left\langle \Psi^{o}_{\alpha}\middle|\hat{x}\middle|\Psi^{o}_{\beta}\right\rangle = \left\langle \frac{\partial\Psi^{o}_{\alpha}}{\partial t}\middle|\hat{x}\middle|\Psi^{o}_{\beta}\right\rangle + \left\langle \Psi^{o}_{\alpha}\middle|\hat{x}\middle|\frac{\partial\Psi^{o}_{\beta}}{\partial t}\right\rangle$$

$$= \frac{i}{\hbar}\left\{\left\langle \hat{H}^{o}\Psi^{o}_{\alpha}|\hat{x}|\Psi^{o}_{\beta}\right\rangle - \left\langle \Psi^{o}_{\alpha}|\hat{x}|\hat{H}^{o}\Psi^{o}_{\beta}\right\rangle\right\}$$ from 1′ realizing $\left\langle \psi^{o}_{\alpha}\right| = \psi^{o*}_{\alpha}$

$$= \frac{i}{\hbar}\left\langle \Psi^{o}_{\alpha}\middle|\hat{H}^{o}\hat{x} - \hat{x}\hat{H}^{o}\middle|\Psi^{o}_{\beta}\right\rangle$$ using the hermetian properties of $\hat{H}^{o}$ and $\hat{x}$ to justify rearrangement

$$= \frac{i}{\hbar}\left\langle \Psi^{o}_{\alpha}\middle|\left[\hat{H}^{o},\ \hat{x}\right]\middle|\Psi^{o}_{\beta}\right\rangle$$

You have learned or can verify by direct manipulation that for $\hat{H}^{o} = \dfrac{\hat{p}^{2}}{2\mu} + U(r)$; $\left[\hat{H}^{o},\ \hat{x}\right] = -\dfrac{i\hbar}{\mu}\hat{p}_{x}$.

Thus the lemma is proven.

To prove the desired relationship between position and momentum transition moments:

(2) $\frac{d}{dt}\left\langle \Psi_\alpha^o|\hat{x}|\Psi_\beta^o \right\rangle = \frac{1}{\mu}\left\langle \Psi_\alpha^o|\hat{p}_x|\Psi_\beta^o \right\rangle$ (from Lemma)

(3) $\left\langle \Psi_\alpha^o|\hat{x}|\Psi_\beta^o \right\rangle = e^{i(E_\alpha^o - E_\beta^o)t/\hbar}\left\langle \psi_\alpha^o|\hat{x}|\psi_\beta^o \right\rangle$

using (2) and (3)

$$\frac{d}{dt}\left[e^{i(E_\alpha^o - E_\beta^o t/\hbar}\left\langle \psi_\alpha^o|\hat{x}|\psi_\beta^o \right\rangle \right] = \frac{i(E_\alpha^o - E_\beta^o)}{\hbar}\left\langle \psi_\alpha^o|\hat{x}|\psi_\beta^o \right\rangle e^{i(E_\alpha^o - E_\beta^o)\,t/\hbar}$$
$$= \frac{1}{\mu}\left\langle \psi_\alpha^o|\hat{p}_x|\psi_\beta^o \right\rangle e^{i(E_\alpha^o - E_\beta^o)\,t/\hbar}$$

thus

(4) $\frac{i(E_\alpha^o - E_\beta^o)}{h}\left\langle \psi_\alpha^o|\hat{x}|\psi_\beta^o \right\rangle = \frac{1}{\mu}\left\langle \psi_\alpha^o|\hat{p}_x|\psi_\beta^o \right\rangle$

(5) by definition $\frac{E_\alpha^o - E_\beta^o}{\hbar} = \omega_{\alpha\beta}$

so that $\boxed{i\mu\omega_{\alpha\beta}\left\langle \psi_\alpha^o|\hat{x}|\psi_\beta^o \right\rangle = \left\langle \psi_\alpha^o|\hat{p}_x|\psi_\beta^o \right\rangle}$ as required.