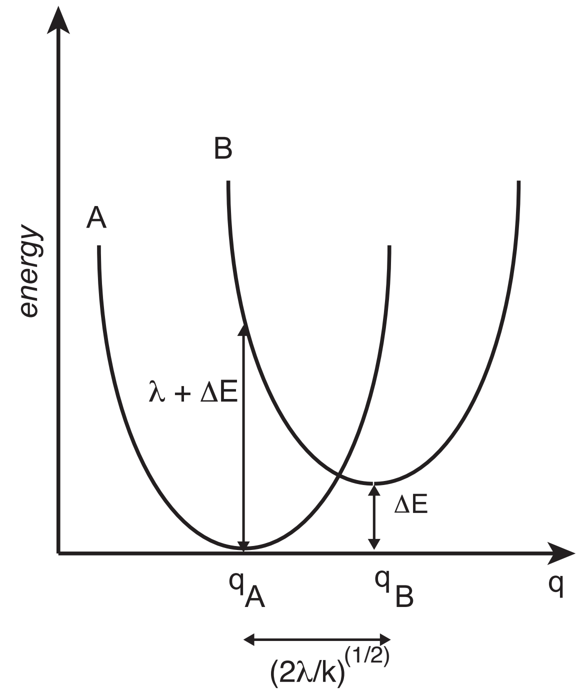
Marcus theory for electron transfer kinetics

Derivation of Eq. 9.53



The potential energies as a function of the "distortion coordinate" q are:

$$V_A(q) = \frac{1}{2}k(q-q_A)^2 \qquad V_B(q) = \frac{1}{2}k(q-q_B)^2 + \Delta E$$

Or

$$V_B - V_A = \Delta V(q) = -k(q-q_A)\left(\frac{2\lambda}{k}\right)^{1/2} + \lambda + \Delta E$$

Now we can find the point q^* where $\Delta V(q^*) = 0$:

$$(q^* - q_A) = \frac{(\lambda+\Delta E)}{(2\lambda k)^{1/2}} = \frac{\lambda(1+\Delta E/\lambda)}{(2\lambda k)^{1/2}}$$

Next, we can compute the activation energy, which is the value of $V_A(q^*)$:

$$V_A(q^*) = \frac{1}{2}k(q^*-q_A)^2 = \frac{1}{2}k\frac{\lambda^2(1+\Delta E/\lambda)^2}{(2\lambda k)} = \frac{\lambda}{4}\left(1+\frac{\Delta E}{\lambda}\right)^2$$

This last is Eq. (9.53) in your text. Note that terms in k cancel.