Pop Quiz 4, Chemistry 481, ~~2~~ 4 Oct 2019. Name: _____

Knowing that the average value of a quantity is defined by

$$\langle A \rangle = \frac{1}{q} \sum_j A_j \exp(-E_j \beta)$$

Determine the mean squared spread in the average energy

$$\delta(E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

in terms of $\langle E \rangle$ and its derivative with respect to β We went over this on Monday 9/30. From the first equation we have

$$\langle E \rangle = \frac{1}{q} \sum_j E_j \exp(-E_j \beta)$$

Differentiating with respect to β gives

$$\begin{aligned} \frac{d\langle E \rangle}{d\beta} &= -\frac{1}{q^2}\frac{dq}{d\beta} \sum_j E_j \exp(-E_j \beta) - \frac{1}{q} \sum_j E_j^2 \exp(-E_j \beta) \\ &= \left[-\frac{1}{q}\frac{dq}{d\beta} \right] \times \frac{1}{q} \sum_j E_j \exp(-E_j \beta) - \frac{1}{q} \sum_j E_j^2 \exp(-E_j \beta) \end{aligned}$$

We know that $\langle E \rangle = -\frac{1}{q}\frac{dq}{d\beta}$ Thus $\langle E \rangle^2 - \langle E^2 \rangle$. So, finally

$$\delta(E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{d\langle E \rangle}{d\beta}$$