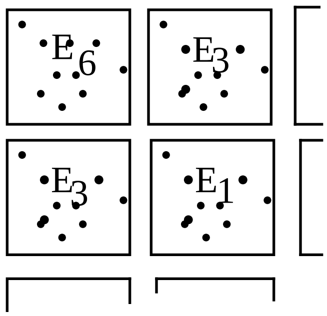
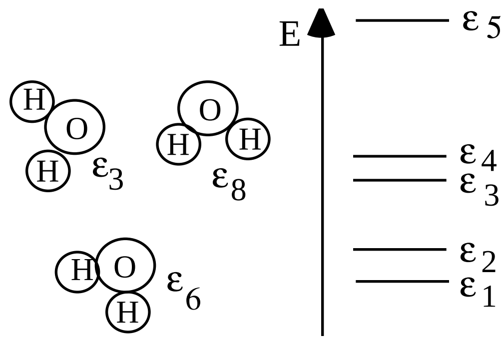
Canonical Ensemble Partition Functions vs. Molecular Partition Functions

Partition functions are in terms of states of a system. Can we write partition functions in terms of states of molecule?



System Energy Levels

vs.



molecule energy levels

$E_{system} = \varepsilon_a + \varepsilon_b + \varepsilon_c + \ldots$

$$Q = \sum_i e^{-\beta E_i} = \sum_i e^{-\beta\varepsilon_{ai}}\ e^{-\beta\varepsilon_{bi}}\ e^{-\beta\varepsilon_{ci}} \ldots\ldots$$

$$Q \overset{?}{=} \sum e^{-\beta\varepsilon_{ai}} \sum e^{-\beta\varepsilon_{bi}} \sum e^{-\beta\varepsilon_{ci}} \ldots\ldots$$

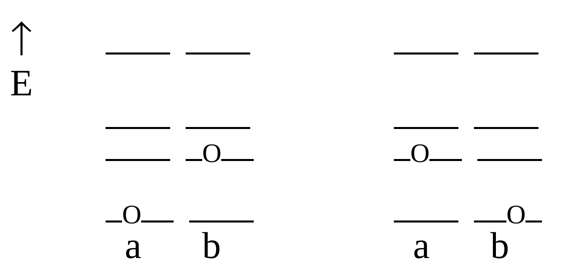
$$= q_a\, q_b\, q_c \ldots$$

Example: two molecules, a and b:

$$Q = (e^{-\beta\varepsilon_{a1}} + e^{-\beta\varepsilon_{a2}} + e^{-\beta\varepsilon_{a3}} + \ldots)(e^{-\beta\varepsilon_{b1}} + e^{-\beta\varepsilon_{b2}} + e^{-\beta\varepsilon_{b3}} + \ldots)$$

Indistinguishable Molecules:

$e^{-\beta\varepsilon_{a1}}\ e^{-\beta\varepsilon_{b2}}$ $\qquad$ $e^{-\beta\varepsilon_{a2}}\ e^{-\beta\varepsilon_{b1}}$



$q_a\, q_b\, q_c \ldots = q^N$

$$Q = \frac{q^N}{N!}$$