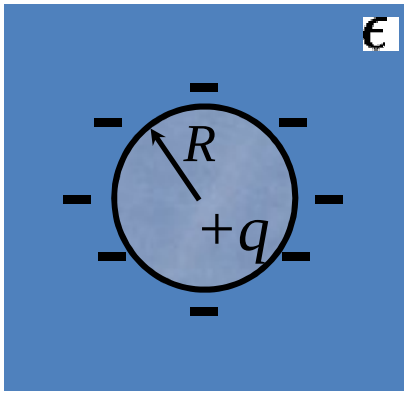
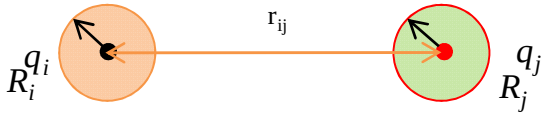
❖ Born solvation model, charging free energy (hydration energy) of a single ion in a spherical cavity.



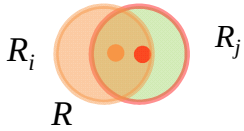
$$\Delta G_{born} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q^2}{R}$$

➢ 2 ions are separated



$$\Delta G_{elec}(r_{ij}\to\infty) = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{q_i^2}{R_i}+\frac{q_j^2}{R_j}\right)-\left(1-\frac{1}{\varepsilon}\right)\frac{q_i q_j}{r_{ij}}$$

➢ 2 ions are superimposed



$$R = \sqrt{R_i R_j}$$

$$\Delta G_{elec}(r_{ij}\to 0) = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{(q_i+q_j)^2}{R} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{q_i^2}{R}+\frac{q_j^2}{R}\right)-\left(1-\frac{1}{\varepsilon}\right)\frac{q_i q_j}{R}$$

❖ Generalized Born model interpolates in between

$$\Delta G_{GB} = -\sum_{i=1}^{N}\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q_i^2}{R_i}-\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q_i q_j}{f_{ij}} \qquad f_{ij} = \sqrt{r_{ij}^2 + R_i R_j e^{-\frac{r_{ij}^2}{4R_i R_j}}}$$

Still et al.(1990) *J. Am. Chem. Soc.* 112, 6127-6129.