The Born Model

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Abstract

In this handout, the solvation model developed by Born will be presented.

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Theory

In Born model, the solvent is represented as a dielectric medium with a dielectric constant ϵ, while the solute is represented as a sphere of a radius R and charge Q in this dielectric medium. Inside the cavity (the solute region), the dielectric constant is 1. For simplicity, we assign the location of the solute ion as the origin of the coordinates. At the inner side of the cavity surface, we have

$$\oint_{\Gamma} \mathbf{E}^- \cdot d\mathbf{S} = 4\pi Q, \tag{1}$$

where $\mathbf{E}^-$ is the electric field generated by the solute charge and the integration is over the cavity surface. Because of the spherical symmetry, the electric field intensity E^- can be expressed as

$$E^- = \frac{4\pi Q}{4\pi R^2} = \frac{Q}{R^2}. \tag{2}$$

Or it can be directly obtained from the definition of electric field.

We draw a pillbox on the cavity surface, and find that

$$\mathbf{E}^- \cdot d\mathbf{S}^- + \mathbf{E}^+ \cdot d\mathbf{S} = 4\pi q, \tag{3}$$

or

$$-E^- + E^+ = 4\pi\sigma, \tag{4}$$

where $\mathbf{E}^+$ and E^+ are the electric field on the outside side of the surface and its intensity, and q and σ are the induced charge and charge density on the cavity surface with in pillbox.

The discontinuity of the electric field across the cavity surface shows|

$$E^- = \epsilon E^+. \tag{5}$$

Combining Eq. 4 and 5, we have

$$\sigma = -\frac{1}{4\pi}\frac{\epsilon - 1}{\epsilon}E^- = -\frac{\epsilon - 1}{\epsilon}\frac{Q}{4\pi R^2}, \tag{6}$$

and the total induced charge in the cavity surface is

$$q = 4\pi R^2\sigma = -\frac{\epsilon - 1}{\epsilon}Q. \tag{7}$$

At any point $\mathbf{r}$ outside the cavity, the electric field is the sum of contributions from the source charge and the induced charge, i. e.

$$\mathbf{E}(\mathbf{r}) = \frac{Q\mathbf{r}}{|\mathbf{r}|^3} + \frac{q\mathbf{r}}{|\mathbf{r}|^3} = \frac{Q\mathbf{r}}{\epsilon|\mathbf{r}|^3}. \tag{8}$$

The correcponding electrostatic potential is

$$\phi = \frac{Q}{r} + \frac{q}{r} = \frac{Q}{\epsilon r}. \tag{9}$$

On the cavity surface, the elctrostatic potential due to the induced charge is

$$\phi_i(R) = \frac{q}{R} = -\frac{\epsilon - 1}{\epsilon}\frac{Q}{R}. \tag{10}$$

Because the induced charge on the surface does not generate electric field in the cavity, the electrostatic potential at the origin due to the induced charge is also

$$\phi_i(0) = -\frac{\epsilon - 1}{\epsilon}\frac{Q}{R}. \tag{11}$$

Therefore, the solvation free energy is

$$\Delta G = \frac{1}{2}\Delta E = -\frac{\epsilon - 1}{2\epsilon}\frac{Q^2}{R}. \tag{12}$$

We can also calculate the solvation free energy from the self energy of the electric field. The self energy of the electric field is

$$W = \frac{1}{2} \cdot \frac{1}{4\pi} \int \mathbf{D} \cdot \mathbf{E} d\mathbf{r}. \tag{13}$$

In vacuum, $\mathbf{D} = \mathbf{E}$. We have

$$W_0 = \frac{1}{2} \cdot \frac{1}{4\pi} \int E_0^2 d\mathbf{r} = \frac{1}{2} \int_0^\infty E_0^2 r^2 dr. \tag{14}$$

In the dielectric medium

$$W_d = \frac{1}{2} \cdot \frac{1}{4\pi} \int \mathbf{D} \cdot \mathbf{E} d\mathbf{r} = \frac{1}{2} \left(\int_0^R E_0^2 r^2 dr + \int_R^\infty \epsilon E^2 r^2 dr \right). \tag{15}$$

The energy difference is

$$
\begin{align}
\Delta W &= W_d - W_0 \tag{16}\\
&= \frac{1}{2}\left(\int_R^\infty \epsilon E^2 r^2 dr - \int_R^\infty E_0^2 r^2 dr\right) \tag{17}\\
&= \frac{1}{2}\int_R^\infty \left(\frac{Q^2}{\epsilon r^4} - \frac{Q^2}{r^4}\right) r^2 dr \tag{18}\\
&= -\frac{1}{2}\frac{\epsilon - 1}{\epsilon}\frac{Q^2}{R} \tag{19}
\end{align}
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