Potential Energy of a distribution of charge in an external potential

Suppose one has N charges in an external potential $\phi(\vec{r})$. By external we mean that the potential is due to charges other than the N of interest. For example, the N charges may be in one molecule while the potential is due to another. The potential energy of the charge distribution consists of two parts: the internal potential energy and that due to the external potential.

$$V = V_{\text{int}} + V_{ext} = \sum_{i>j}^{N} \frac{q_i q_j}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i=1}^{N} q_i \phi(\vec{r}_i)$$

and we will be concerned only with the external contribution. Often the external potential will be slowly varying over the spatial extension of the charge distribution and it will make sense to expand the potential in a Taylor series about a point internal to the charge distribution. Often our charge distribution is a molecule, i.e., a collection of nuclei and electrons. If the point we expand about is $\vec{R}$ we can locate the position of the i$^{\text{th}}$ particle as $\vec{r}_i = \vec{R} + \xi_i$ and then

$$V_{ext} = \sum_{i=1}^{N} q_i \phi(\vec{R} + \vec{\xi}_i)$$

Consider a representative potential term $\phi(\vec{R} + \vec{\xi})$ and perform a Taylor series expansion about $\vec{\xi} = 0$.

$$\phi(\vec{R} + \vec{\xi}) = \phi(\vec{R}) + \sum_{\alpha=x}^{z} \left(\frac{\partial \phi}{\partial \xi_\alpha} \right)_0 \xi_\alpha + \frac{1}{2} \sum_{\alpha=x}^{z} \sum_{\beta=x}^{z} \left(\frac{\partial^2 \phi}{\partial \xi_\alpha \, \partial \xi_\beta} \right)_0 \xi_\alpha \xi_\beta + \ldots$$

The x, y, z coordinates of the particle are $\xi_x, \xi_y \;\&\; \xi_z$ and we will use $R_x, R_y, \& R_z$ for the x, y, z coordinates of the point $\vec{R}$. The Greek indices $\alpha \,\&\, \beta$ take on the values x, y and z. We will use the Einstein summation convention, which assumes that repeated a Greek suffix implies summation over the x, y, and z values of that suffix. So the above equation becomes

$$\phi(\vec{R} + \vec{\xi}) = \phi(\vec{R}) + \left(\frac{\partial \phi}{\partial \xi_\alpha} \right)_0 \xi_\alpha + \frac{1}{2} \left(\frac{\partial^2 \phi}{\partial \xi_\alpha \, \partial \xi_\beta} \right)_0 \xi_\alpha \xi_\beta + \frac{1}{3!} \left(\frac{\partial^3 \phi}{\partial \xi_\alpha \, \partial \xi_\beta \, \partial \xi_\gamma} \right)_0 \xi_\alpha \xi_\beta \xi_\gamma +$$

The various derivatives with respect to ξ_α, ξ_β & ξ_γ, may be written in terms of derivatives WRT R_α, R_β & R_γ as

$$\left(\frac{\partial \phi}{\partial \xi_\alpha}\right)_0 = \frac{\partial \phi}{\partial R_\alpha} \equiv \nabla_\alpha \phi = -F_\alpha$$

$$\left(\frac{\partial^2 \phi}{\partial \xi_\alpha \partial \xi_\beta}\right)_0 = \frac{\partial^2 \phi}{\partial R_\alpha \partial R_\beta} \equiv \nabla_{\alpha\beta} \phi = -F_{\alpha\beta}$$

$$\left(\frac{\partial^3 \phi}{\partial \xi_\alpha \partial \xi_\beta \partial \xi_\gamma}\right)_0 = \frac{\partial^3 \phi}{\partial R_\alpha \partial R_\beta \partial R_\gamma} \equiv \nabla_{\alpha\beta\gamma} \phi = -F_{\alpha\beta\gamma}$$

We have identified the first derivative of the potential at the point R_α with the negative of the electric field $-F_\alpha$ at this point due to the external potential, the second derivative with the negative of the field gradient $-F_{\alpha\beta}$ at this point, the third derivative with the negative of the gradient of the electric field gradient, $-F_{\alpha\beta\gamma}$, etc. With this very compact notation the potential becomes

$$\phi(\vec{R} + \vec{\xi}) = \phi(\vec{R}) - \xi_\alpha F_\alpha + \frac{1}{2}\xi_\alpha \xi_\beta F_{\alpha\beta} + \frac{1}{3!}\xi_\alpha \xi_\beta \xi_\gamma F_{\alpha\beta\gamma} +$$

Inserting this in the expression for V_{ext} gives

$$V_{ext} = Q\phi(\vec{R}) - \mu_\alpha F_\alpha - \frac{1}{2} A_{\alpha\beta} F_{\alpha\beta} - \frac{1}{3} W_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - \cdots$$

Where

$$Q = \sum_{i=1}^{N} q_i$$

is the total charge of the *N* point charges, often called the first moment of the charge distribution.

$$\mu_\alpha = \sum_{i=1}^{N} q_i \xi_{i\alpha}$$

is the α component of the second moment of the charge distribution,

$$A_{\alpha\beta} = \sum_{i=1}^{N} q_i \xi_{i\alpha} \xi_{i\beta}$$

is the $\alpha\beta$ component of the third moment of the charge distribution,

$$W_{\alpha\beta\gamma} = \sum_{i=1}^{N} q_i \xi_{i\alpha} \xi_{i\beta} \xi_{i\gamma}$$

is the $\alpha\beta\gamma$ component of the fourth moment of the charge distribution, and so on. Note that if the potential does not vary over the spatial extension of the charge distribution, i.e. all derivatives are zero, then the potential energy of the charge distribution is simply the familiar

$$V_{ext} = Q\phi(\vec{R})$$

This is also the expression for the potential energy of a point charge Q in an electrostatic potential, which makes sense since a point charge has no spatial extension and there would be no spatial dependence of the potential over the extent of the charge. Observe that this means that the potential energy of a neutral charge distribution is zero in a constant potential.

Exercise

Calculate the electrostatic potential, electric field and electric field gradient in the SI and atomic system of units at the point $\vec{R} = \hat{x} + 2\hat{y} + 3\hat{z}$ *due to a proton at the origin. The vector* $\vec{R}$ *is in Angstroms.*