# ESP Transition Charges

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We are looking at the Merz-Kollman (MK) method which involves fitting atomic charges to reproduce the electrostatic potential (ESP) generated by a Transition Density. By definition, the sum of transition charges should be zero, irrespective of the charge of the molecule :

$$\sum_i q_i^{Tr} = 0 \tag{1}$$

Given grid points $\{\mathbf{R}_\mu\}$ with corresponding potentials $\{\Phi_\mu^{\mathrm{QM}}\}$. and atomic positions $\{\mathbf{R}_i\}$. We want to solve for the atomic charges $\{q_i\}$ such that the electrostatic potential is reproduced and the sum of the charges is zero.

## Mean Square Deviation (MSD)

The MSD between the quantum mechanical potential ($\Phi_\mu^{\mathrm{QM}}$) and the potential from the atomic charges ($\phi_\mu(\{q_i\})$) is given by:

$$\mathrm{MSD} = \sum_\mu \left(\Phi_\mu^{\mathrm{QM}} - \phi_\mu(\{q_i\})\right)^2 = \sum_\mu \left(\Phi_\mu^{\mathrm{QM}} - \sum_i \frac{q_i}{|\mathbf{R}_\mu - \mathbf{R}_i|}\right)^2 \tag{2}$$

$$\mathrm{MSD} = \sum_\mu \left(\left(\Phi_\mu^{\mathrm{QM}}\right)^2 - 2\Phi_\mu^{(\mathrm{QM})} \sum_i \frac{q_i}{|\mathbf{R}_\mu - \mathbf{R}_i|} + \left(\sum_i \frac{q_i}{|\mathbf{R}_\mu - \mathbf{R}_i|}\right)^2\right) \tag{3}$$

$$\mathrm{MSD} = \sum_\mu \left(\Phi_\mu^{\mathrm{QM}}\right)^2 - 2\sum_\mu \Phi_\mu^{\mathrm{QM}} \sum_i \frac{q_i}{|\mathbf{R}_\mu - \mathbf{R}_i|} + \sum_\mu \left(\sum_i \frac{q_i}{|\mathbf{R}_\mu - \mathbf{R}_i|}\right)^2 \tag{4}$$

With :

$$c = \sum_\mu \left(\Phi_\mu^{\mathrm{QM}}\right)^2 \quad ; \quad e_i = \sum_\mu \frac{\Phi_\mu^{\mathrm{QM}}}{|\mathbf{R}_\mu - \mathbf{R}_i|} \quad ; \quad G_{ij} = \sum_\mu \frac{1}{|\mathbf{R}_\mu - \mathbf{R}_i||\mathbf{R}_\mu - \mathbf{R}_j|} \tag{5}$$

We have the Simplified Matrix Notation :

$$\mathrm{MSD} = \mathbf{q}^T\mathbf{G}\mathbf{q} - 2\mathbf{e}^T\mathbf{q} + c \tag{6}$$

## Lagrangian with Total Charge Constraint

To impose the constraint that the total charge is zero, we add the constraint to the Lagrangian:

$$L = \frac{1}{2}\left(\mathbf{q}^T\mathbf{G}\mathbf{q} - 2\mathbf{e}^T\mathbf{q} + c\right) + \lambda\left(\sum_i q_i - Q\right) \tag{7}$$

where $Q = 0$ in our case.

## Analytical Expression

Applying the constraint $\sum_i q_i = Q$, we solve for $\lambda$:

$$\sum_i q_i = \sum_i G_{ij}^{-1} e_j - \lambda \sum_{i,j} G_{ij}^{-1} = 0 \tag{8}$$

$$\lambda = \frac{\sum_i G_{ij}^{-1} e_j}{\sum_{i,j} G_{ij}^{-1}} \tag{9}$$

Finally, we calculate the charges:

$$q_i = G_{ij}^{-1} e_j - \lambda \sum_j G_{ij}^{-1} \tag{10}$$

with $\lambda$ given by the previous expression.

## Matrix Expression

$$\begin{bmatrix} G & 1 \\ \mathbf{1}^T & 0 \end{bmatrix} \begin{bmatrix} \mathbf{q} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{e} \\ Q \end{bmatrix} \tag{11}$$

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{b} \implies \mathbf{x} = \mathbf{A}^{-1} \cdot \mathbf{b} \tag{12}$$