Minimization with QEq (Ray Shan, Sandia)

The total energy of a variable charge potential can be written as:

$$E_T = E(q, r) + E(r)$$

so the derivative with respect to Cartesian coordinates of atomic positions is:

$$-F = \frac{dE_T}{dr} = \sum_i \frac{\partial E(q, r)}{\partial q_i} \frac{\partial q_i}{\partial r} + \frac{\partial E(r)}{\partial r}$$

All derivatives $\partial E(q, r)/\partial q_i$ are equal at charge equilibrium (to μ, the electronegativity) since the charges q_i are each chosen to minimize the energy. So with some change in the order of summation and differentiation, the terms involving derivatives of q_i can be re-written as:

$$\sum_i \frac{\partial E(q, r)}{\partial q_i} \frac{\partial q_i}{\partial r} = \mu \frac{\partial}{\partial r} \sum_i q_i$$

Since $\sum_i q_i = 0$ due to enforced global charge neutrality, the whole term vanishes and no $\partial q/\partial r$ terms appear in force expressions. The derivative of the total energy of a variable charge with respect to positions is left with

$$-F = \frac{dE_T}{dr} = \frac{\partial E(r)}{\partial r}$$