I. MULLIKEN CHARGES

The Mulliken charges are defined as

$$Q_A = \sum_{\mu \in A} \sum_{\nu} P^{\mu\nu} S_{\mu\nu} \tag{1}$$

Their full derivatives with respect to nuclear displacements are

$$Q_A^{(x)} = \sum_{\mu \in A} \sum_{\nu} P^{\mu\nu,(x)} S_{\mu\nu} + \sum_{\mu \in A} \sum_{\nu} P^{\mu\nu} S_{\mu\nu}^{(x)} \tag{2}$$

where the second term is called the M-derivative. The first term depends on the density response,

$$P^{(x)} = -\frac{1}{2} C C^{\dagger} S^{(x)} P + C_v \Theta^{(x)} C_o^{\dagger} \tag{3}$$

which include an overlap derivative component and an orbital relaxation component. So the nuclear gradient of Mulliken charges are:

$$Q_A^{(x)} = Q_{A,PS}^{(x)} + Q_{A,PO}^{(x)} + Q_{A,M}^{(x)} \tag{4}$$

$$Q_{A,PS}^{(x)} = -\frac{1}{2} \sum_{\mu \in A} \sum_{\nu} \left[C C^{\dagger} S^{(x)} P \right]^{\mu\nu} S_{\mu\nu} \tag{5}$$

$$Q_{A,OR}^{(x)} = \sum_{\mu \in A} \sum_{\nu} \left[C_v \Theta^{(x)} C_o^{\dagger} \right]^{\mu\nu} S_{\mu\nu} \tag{6}$$

$$Q_{A,M}^{(x)} = \sum_{\mu \in A} \sum_{\nu} P^{\mu\nu} S_{\mu\nu}^{(x)} \tag{7}$$

When Mulliken charges are employed in an implicit solvent model (I am not aware of any) or QM/MM model, the orbital relaxation component ($Q_{A,OR}^{(x)}$) can be ignored in an energy gradient calculation, while the overlap derivative component ($Q_{A,PS}^{(x)}$) is automatically folded into the Pulay term through the energy weighted density matrix. Only the M-derivatives ($Q_{A,M}^{(x)}$) need to be added explicitly.

If, for any reason, full gradient is needed, we can solve CPSCF equation for the 3*NAtoms orbital responses (3 for each atom). But we might be able to save a little bit time by solving for only ONE response for each atom. This can be done by rewritten as the orbital relaxation

component of the gradient as

$$\begin{aligned} Q^{(x)}_{A,PO} &= \sum_{\mu\in A}\sum_{\nu}\sum_{ai} C_{\mu a}\Theta^{(x)}_{ai}C_{\nu i}S_{\mu\nu} \\ &= \sum_{\mu\in A}\sum_{\nu}\sum_{ai} C_{\mu a}\sum_{bj}\left[\left(E^{\Theta\Theta}\right)^{-1}\right]_{ai,bj} h^{(x)}_{bj}C_{\nu i}S_{\mu\nu} \\ &= \sum_{bj} h^{(x)}_{bj}\sum_{ai}\left[\left(E^{\Theta\Theta}\right)^{-1}\right]_{ai,bj}\left[\sum_{\mu\in A}\sum_{\nu} C_{\mu a}S_{\mu\nu}C_{\nu i}\right] \\ &= \sum_{bj} h^{(x)}_{bj}\sum_{ai}\left[\left(E^{\Theta\Theta}\right)^{-1}\right]_{ai,bj} S_{A,ai} \\ &= \sum_{bj} h^{(x)}_{bj} Z_{A,bj} \end{aligned} \tag{8}$$

where

$$S_{A,ai} = \sum_{\mu\in A}\sum_{\nu} C_{\mu a}S_{\mu\nu}C_{\nu i} \tag{9}$$

is the overlap between a normal occupied orbital (i) and a truncated virtual orbital (a), which has only contributions from basis functions on atom A. $Z_{A,bj}$ is the corresponding z vector,

$$Z_{A,bj} = \sum_{ai}\left[\left(E^{\Theta\Theta}\right)^{-1}\right]_{ai,bj} S_{A,ai} \tag{10}$$