Estimation of the Bias Potential and Charge Transfer Energy in Constrained Density Functional Theory Calculations

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Given a weight matrix, W_p, using a population scheme, we can use its AO representation to obtain the unbiased population from the unbiased density matrix ($P^{(0)}$)

$$Q_p^0 = W_{p,ao} \cdot P^{(0)} + (\text{nuclear contribution}) \tag{1}$$

We can convert the weight matrix into the MO representation (V $\times$ O), and compute its corresponding z vector,

$$z_p = (E_{\Theta\Theta})^{-1} W_{p,mo} \tag{2}$$

From the z vector, we can compute the corresponding density matrix change (i.e. Fock build is incremented with one unit of the weight matrix)

$$\Delta P_p = C_v z_p C_o^\dagger + C_o z_p^\dagger C_v^\dagger \tag{3}$$

and population change

$$\Delta Q_p = \Delta P_p \cdot W_{p,ao} \tag{4}$$

From that, we can estimate the required bias potential for achieving a zero-charge fragment,

$$\lambda_p = -\frac{Q_p^0}{\Delta Q_p} \tag{5}$$

and the energy charge for this charge constraint is

$$E(\lambda_p) = \frac{1}{2} \ \ \lambda_p^2 \ \ (z_p \cdot W_{p,mo}) \tag{6}$$