Hierarchical Multipole Expansion

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I. MONOPOLE

Since the delta RESP fitting method has been proved to be a quite stable method in obtaining atomic charges[1], it is reasonable to extend this idea to multipole expansion. The basic idea is to fit the multipole components to the residual electrostatic potential with the contributions from the lower level multipoles removed. For a molecule with M_{atom}, we can generate electrostatic potential V_j on N_{grid} pre-chosen grids with the electron density at high level quantum mechanical calculations. Suppose we have an initial guess of the monopoles $\{q_i\}$ distributed on nuclei, the contributions to the total electrostatic potential from these charges is

$$\hat{V}_j = \sum_{i=1}^{M_{atom}} \frac{q_i}{r_{ij}}. \tag{1}$$

Then we want to acquire perturbations $\{\delta q_i\}$ to these intial guess of monopoles that can minimize the deviation of electrostatic potential on these grids, that is to minimize the figure-of-merit function

$$\chi^2 = \sum_{j=1}^{N_{grid}} \left(V_j - \hat{V}_j - \sum_{i=1}^{M_{atom}} \frac{\delta q_i}{r_{ij}} \right)^2 \tag{2}$$

with respect to $\{\delta q_i\}$. $V_j - \hat{V}_j$ is the residual ESP (V_j^{res}) after the contribution of the initial guess of the monopole. Therefore for any δq_k

$$\begin{aligned} 0 &= \frac{\partial \chi^2}{\partial \delta q_k} \\ &= \sum_{j=1}^{N_{grid}} 2 \left(V_j^{res} - \sum_{i=1}^{M_{atom}} \frac{\delta q_i}{r_{ij}} \right) \frac{1}{r_{kj}}, \end{aligned}$$

in which r_{ij} is the distance between the ith atom and the jth grid. So we have

$$\sum_{i=1}^{M_{atom}} \sum_{j=1}^{N_{grid}} \frac{\delta q_i}{r_{ij} r_{kj}} = \sum_{j=1}^{N_{grid}} \frac{V_j^{res}}{r_{kj}}. \tag{3}$$

In order to mitigate the impact of numerical difficulty to $\{\delta q_i\}$, we apply a restraint on each δq_i as

$$\chi^2_{rstr} = a \sum_i W_i \delta q_i^2 \tag{4}$$

in a harmonic form or alternatively

$$\chi^2_{rstr} = a \sum_i W_i \left(\sqrt{\delta q_i^2 + b^2} - b \right) \tag{5}$$

in a hyperbolic form, in which a is the strength of the restraint and W_i is the weighting factor for δq_i. In the original implementation of RESP, W_i is unit for all the charges. But in our implementation, W_i is inversely proportional to the inital guess of the monopole q_i, i. e.

$$W_i \propto (1/q_i)^2 . \tag{6}$$

The charge perturbations do not introduce net charge into the system, therefore

$$\sum_{j=1}^{N_{atom}} \delta q = 0 \tag{7}$$

We can write Eq. 3, together with the harmonic restraint and the Lagrange condition, in a matrix form as

$$\mathbf{A} \delta \mathbf{Q} = \mathbf{B}, \tag{8}$$

where

$$A_{ij} = \sum_{k=1}^{N_{grid}} \frac{1}{r_{ik} r_{jk}} - a W_i \delta_{ij}, \tag{9}$$

and

$$B_i = \sum_{k=1}^{N_{grid}} \frac{V_k^{res}}{r_{ki}} + \lambda, \tag{10}$$

where λ is the Lagrange multiplier, which can be set to zero.

II. DIPOLE

Although the electrostatic potential on the grids produced by the discret charges can be improved with the existence of the charge perturbations, there is in general still some difference between the QM ESP and the MM ESP. This difference cannot be further reduced by monopoles if no extra charge points are introduced. Therefore, we incorporate higher level of multipoles for each atom to further improve the MM ESP. We introduce atomic dipole first. Theoretically, one can fit the monopole (perturbation) and the dipole moments simultaneously as in the implementation of OPEP. However, as we know that the electrostatic potential generated by dipole decays one-order faster ($1/r^2$) than that by monopole ($1/r$). It will introduce numerical difficulty in deternining the dipole moments. It is a good idea to fit the dipole moment to the residual ESP (with the contributions of both the initial guess of monopole and the perturbations removed) again. The figure-of-merit function reads

$$\chi^2 = \sum_{j=1}^{N_{grid}} \left(V_j^{res} - \sum_{i=1}^{M_{atom}} \sum_{\alpha=x,y,z} \frac{\mu_i^\alpha \cdot R_{ij}^\alpha}{(R_{ij})^3} \right)^2 + a \sum_{i=1}^{M_{atom}} \sum_{\alpha=x,y,z} \left(\mu_i^\alpha - \mu_{i0}^\alpha\right)^2 , \tag{11}$$

where R_{ij} is the length of the vector pointing from the ith atom to the jth grid, and R_{ij}^α is its α component in Cartesian space, μ_{i0}^α is the initial guess of μ_i^α, which can be taken from GDMA analysis or simply set it to zero. Minimization of χ^2 with respect to μ_k^β leads to

$$\begin{aligned} 0 &= \frac{\partial \chi^2}{\partial \mu_k^\beta} \\ &= \sum_{j=1}^{N_{grid}} 2 \left(V_j^{res} - \sum_{i=1}^{M_{atom}} \sum_{\alpha=x,y,z} \frac{\mu_i^\alpha \cdot R_{ij}^\alpha}{(R_{ij})^3} \right) \cdot \frac{R_{kj}^\beta}{(R_{kj})^3} + 2a \cdot (\mu_k^\beta - \mu_{k0}^\beta). \end{aligned}$$

Then we have

$$\sum_{i=1}^{M_{atom}} \sum_{\alpha=x,y,z} \sum_{j=1}^{N_{grid}} \left(\frac{R_{ij}^\alpha \cdot R_{kj}^\beta}{(R_{ij} \cdot R_{kj})^3} - a \cdot \delta_{ik}\delta_{\alpha\beta} \right) \mu_i^\alpha = \sum_{j=1}^{N_{grid}} \frac{V_j^{res} \cdot R_{kj}^\beta}{(R_{kj})^3} + a\mu_{k0}^\beta. \tag{12}$$

The matrix representation for Eq. 12 is

$$\mathbf{AD} = \mathbf{B}. \tag{13}$$

The dimension of $\mathbf{A}$ is $3M_{atom} \times 3M_{atom}$.

III. QUADRUPOLE

The residual ESP after wiping out the contributions from monopole and dipole moments is used to fit the quadrupole. The figure-of-merit function reads

$$
\begin{aligned}
\chi^2 &= \sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j \right)^2 \\
&= \sum_{j=1}^{N_{grid}} \left(V_j^{res} - \sum_{i=1}^{M_{atom}} \sum_{\alpha,\beta} \frac{Q_i^{\alpha,\beta} R_{ij}^{\alpha} R_{ij}^{\beta}}{\left| R_{ij} \right|^5} \right)^2 ,
\end{aligned}
\tag{14}
$$

in which $Q_i^{\alpha,\beta}$ is the α, β component of the quadrupole moment of atom i in Cartesian-tensor form. Minimizing χ^2 with respect to $Q_k^{\alpha\prime,\beta\prime}$ gives 0, i. e.,

$$
\begin{aligned}
0 &= \frac{\partial \chi^2}{\partial Q_k^{\alpha\prime,\beta\prime}} \\
&= 2 \sum_{j=1}^{N_{grid}} \left(V_j^{res} - \sum_{i=1}^{M_{atom}} \sum_{\alpha,\beta} \frac{Q_i^{\alpha,\beta} R_{ij}^{\alpha} R_{ij}^{\beta}}{\left| R_{ij} \right|^5} \right) \frac{R_{kj}^{\alpha\prime} R_{kj}^{\beta\prime}}{\left| R_{kj} \right|^5}
\end{aligned}
$$

Then we have

$$
\sum_{i=1}^{M_{atom}} \sum_{\alpha,\beta} \sum_{j=1}^{N_{grid}} \frac{R_{ij}^{\alpha} R_{ij}^{\beta} R_{kj}^{\alpha\prime} R_{kj}^{\beta\prime}}{\left| R_{ij} \right|^5 \left| R_{kj} \right|^5} Q_i^{\alpha,\beta} = \sum_{j=1}^{N_{grid}} \frac{V_j^{res} R_{kj}^{\alpha\prime} R_{kj}^{\beta\prime}}{\left| R_{kj} \right|^5} . \tag{15}
$$

However, the quadrupole matrix in Cartesian space ($Q^{\alpha,\beta}$) is symmetry and traceless and there are only 5 degrees of freedom for each atom. Therefore, we should add 4 constraints for each atom to Eq. 14 as

$$
\begin{aligned}
Q_i^{\alpha,\beta} &= Q_i^{\beta,\alpha} , \\
\sum_{\alpha=x,y,z} Q_i^{\alpha,\alpha} &= 0.
\end{aligned}
$$

A more convenient way to do is to use spherical-tensor representation of quadrupoles.

IV. QUADRUPOLE IN SPHERICAL-TENSOR FORM

We rewrite Eq.14 as

$$
\chi^2 = \sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j \right)^2 ,
$$

$$\hat{V}_j = \sum_{i=1}^{M_{atom}} \frac{Q_i^{20}\left(\frac{3}{2}Z_{ij}^2 - \frac{1}{2}R_{ij}^2\right) + Q_i^{21c}\sqrt{3}X_{ij}Z_{ij} + Q_i^{21s}\sqrt{3}Y_{ij}Z_{ij} + Q_i^{22c}\frac{\sqrt{3}}{2}\left(X_{ij}^2 - Y_{ij}^2\right) + Q_i^{22s}\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5}.$$

Then we have

$$\frac{\partial\chi^2}{\partial Q_k^{20}} = 2\sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j\right) \frac{3Z_{kj}^2 - R_{kj}^2}{2R_{kj}^5},$$

$$\frac{\partial\chi^2}{\partial Q_k^{21c}} = 2\sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j\right) \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5},$$

$$\frac{\partial\chi^2}{\partial Q_k^{21s}} = 2\sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j\right) \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5},$$

$$\frac{\partial\chi^2}{\partial Q_k^{22c}} = 2\sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j\right) \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5},$$

$$\frac{\partial\chi^2}{\partial Q_k^{22s}} = 2\sum_{j=1}^{N_{grid}} \left(V_j^{res} - \hat{V}_j\right) \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5}.$$

The least-square equation reads

$$\mathbf{AQ} = \mathbf{B},$$

where

$$\mathbf{B} = \begin{bmatrix} \sum_{j=1}^{N_{grid}} \frac{3Z_{kj}^2 - R_{kj}^2}{2R_{kj}^5} V_j^{res} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} V_j^{res} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} V_j^{res} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} V_j^{res} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} V_j^{res} \end{bmatrix},$$

and

$$\mathbf{A}_k^{20} = \begin{cases} \sum_{j=1}^{N_{grid}} \frac{\left(3Z_{ij}^2 - R_{ij}^2\right)}{2R_{ij}^5} \frac{\left(3Z_{kj}^2 - R_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Z_{ij}}{R_{ij}^5} \frac{\left(3Z_{kj}^2 - R_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{ij}Z_{ij}}{R_{ij}^5} \frac{\left(3Z_{kj}^2 - R_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{ij}^2 - Y_{ij}^2\right)}{2R_{ij}^5} \frac{\left(3Z_{kj}^2 - R_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5} \frac{\left(3Z_{kj}^2 - R_{kj}^2\right)}{2R_{kj}^5} \end{cases}$$

$$\mathbf{A}_k^{21c} = \begin{cases} \sum_{j=1}^{N_{grid}} \frac{\left(3Z_{ij}^2 - R_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{ij}^2 - Y_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Z_{kj}}{R_{kj}^5} \end{cases}$$

$$\mathbf{A}_k^{21s} = \begin{cases} \sum_{j=1}^{N_{grid}} \frac{\left(3Z_{ij}^2 - R_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{ij}^2 - Y_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5} \frac{\sqrt{3}Y_{kj}Z_{kj}}{R_{kj}^5} \end{cases}$$

$$\mathbf{A}_k^{22c} = \begin{cases} \sum_{j=1}^{N_{grid}} \frac{\left(3Z_{ij}^2 - R_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{ij}^2 - Y_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5} \frac{\sqrt{3}\left(X_{kj}^2 - Y_{kj}^2\right)}{2R_{kj}^5} \end{cases}$$

$$\mathbf{A}_k^{22s} = \begin{cases} \sum_{j=1}^{N_{grid}} \frac{\left(3Z_{ij}^2 - R_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}Y_{ij}Z_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}\left(X_{ij}^2 - Y_{ij}^2\right)}{2R_{ij}^5} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} \\ \sum_{j=1}^{N_{grid}} \frac{\sqrt{3}X_{ij}Y_{ij}}{R_{ij}^5} \frac{\sqrt{3}X_{kj}Y_{kj}}{R_{kj}^5} \end{cases}$$

[1] Zeng, J.; Duan, L. L.; Zhang, J. Z. H.; Mei, Y., "A numerically stable restrained electrostatic potential charge fitting method", Journal of Computational Chemistry, **34**, 847-853 (2013).