Extrapolation of Charge Density: Ver. 1.0

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August 16, 2007

Let us consider an extrapolation $\bar{\mathbf{x}}_{n+1}$ of the coordinate at the $(n+1)$th molecular dynamic or geometry optimization step [1, 2] by a linear combination of the previous coordinates $\{\mathbf{x}_m\}$ as

$$\bar{\mathbf{x}}_{n+1} = \sum_{m=n-(p-1)}^{n} \alpha_m \mathbf{x}_m, \tag{1}$$

where for p three is an optimum choice in many cases. To fit well the coordinate $\bar{\mathbf{x}}_{n+1}$ to the real coordinate $\mathbf{x}_{n+1}$, we consider the minimization of a function F:

$$F = |\bar{\mathbf{x}}_{n+1} - \mathbf{x}_{n+1}|^2 - \lambda \left(1 - \sum_{m=n-(p-1)}^{n} \alpha_m \right) \tag{2}$$

with respect to $\{\alpha_i\}$ and λ. The conditions $\frac{\partial F}{\partial \alpha_m} = 0$ and $\frac{\partial F}{\partial \lambda} = 0$ leads to

$$\begin{pmatrix} \langle \mathbf{x}_{(n-(p-1))} | \mathbf{x}_{(n-(p-1))} \rangle & \cdots & \cdots & 1 \\ \cdots & \cdots & \cdots & 1 \\ \cdots & \cdots & \langle \mathbf{x}_n | \mathbf{x}_n \rangle & \cdots \\ 1 & 1 & \cdots & 0 \end{pmatrix} \begin{pmatrix} \alpha_{(n-(p-1))} \\ \alpha_{(n-(p-1)+1)} \\ \cdot \\ \frac{1}{2}\lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdot \\ 1 \end{pmatrix}. \tag{3}$$

By solving the linear equation, we may have an optimum choice of a set of $\{\alpha_m\}$. Then, it is assumed that the difference charge density $\Delta\rho_i^{(\mathrm{out})}$ can be extrapolated well by the same set of coefficients $\{\alpha_m\}$ as

$$\rho_{n+1}^{(\mathrm{in})} = \rho_{n+1}^{(\mathrm{atom})} + \sum_{m=n-(p-1)}^{n} \alpha_m \Delta\rho_m^{(\mathrm{out})}, \tag{4}$$

where $\rho_{n+1}^{(\mathrm{atom})}$ is given by the superposition of atomic charge densities at $\mathbf{x}_{n+1}$. Using Eq. (4) it can be possible to estimate a good input charge density at the $(n+1)$th step in molecular dynamic simulations or geometry optimizations.

References

[1] T. A. Arias, M. C. Payne, and J. D. Joannopoulos, Phys. Rev. B **45**, 1538 (1992).

[2] D. Alfe, Comp. Phys. Commun. **118**, 32 (1999).