Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Line-Search Method of Optimizing the Hamiltonian for Ensemble DFT

The Hamiltonian is optimized by a line-search algorithm in the space of Hamiltonian elements[1] for a fixed set of NGWFs. Let $\tilde{\mathbf{H}}^{(m)}$ denote the Hamiltonian that is formed from the m-th electron density, $n^{(m)}$, whose molecular orbitals were in turn solved from a trial Hamiltonian, $\mathbf{H}^{(m)}$, as

$$\mathbf{H}^{(m)}\mathbf{M}^{(m)} = \mathbf{S}\mathbf{M}^{(m)}\varepsilon^{(m)} \tag{1}$$

where $\mathbf{H}^{(m)}$ and $\tilde{\mathbf{H}}^{(m)}$ are the matrix representations of the corresponding Hamiltonians in NGWFs, $\mathbf{S}$ is the overlap matrix of NGWFs, $\mathbf{M}^{(m)}$ is the coefficient matrix for the molecular orbitals expanded in NGWFs, and $\varepsilon^{(m)}$ is the diagonal matrix of orbital energies. According to the line-search algorithm, the next Hamiltonian is determined by

$$\mathbf{H}^{(m+1)} = \mathbf{H}^{(m)} + \lambda\Delta^{(m)} \tag{2}$$

with the definition of

$$\Delta^{(m)} \equiv \tilde{\mathbf{H}}^{(m)} - \mathbf{H}^{(m)} \tag{3}$$

and λ is a damping parameter fitted against a polynomial such that the Helmholtz free energy is minimized[1,2]. Equation (2) can then be rewritten as

$$\mathbf{H}^{(m+1)} = (1-\lambda)\mathbf{H}^{(m)} + \lambda\tilde{\mathbf{H}}^{(m)} \tag{4}$$

The line-search algorithm performs the iterations over m until the Liouville equation is satisfied when the commutator, $\left[\tilde{\mathbf{H}}^{(m)}, \mathbf{K}^{(m)}\right]$, attains zero, with the definition of the elements of the density kernel, $\mathbf{K}$, as

$$K^{ij} = \sum_{k}^{N_{\text{elec}}} M^{i}{}_{k} f_k \left(\mathbf{M}^{\dagger}\right)_{k}{}^{j} \tag{5}$$

Derivation of Weighted Orthogonalization

Weighted orthogonalization (WO) was developed by West[3] for orthogonalizing orbitals with arbitrary weights. Starting with $\mathbf{P} = \left(|p_1\rangle \ |p_2\rangle \ \cdots \right)$ as a nonorthogonal and normalized matrix of orbitals, it is preliminarily orthogonalized to yield $\mathbf{Q}' = \left(|q_1'\rangle \ |q_2'\rangle \ \cdots \right)$, which is an intermediate matrix that is orthogonal. Transformation of $\mathbf{Q}'$ to $\mathbf{Q}$ is performed by sweeps of 2-by-2 rotations such that the weighted overlap sum, OVLPS, is maximized:

$$\text{OVLPS} = \sum_k w_k \langle p_k | q_k \rangle \tag{6}$$

where w_k is the weight associated with $|p_k\rangle$. $\mathbf{Q}$ is the unknown and can be expressed in terms of the known intermediate matrix, $\mathbf{Q}'$. For a pair of orbitals, the rotation angle, θ_{ij}, is evaluated from

$$\begin{pmatrix} |q_i\rangle & |q_j\rangle \end{pmatrix} = \begin{pmatrix} |q_i'\rangle & |q_j'\rangle \end{pmatrix} \begin{pmatrix} \cos\theta_{ij} & -\sin\theta_{ij} \\ \sin\theta_{ij} & \cos\theta_{ij} \end{pmatrix}^{\mathrm{T}} \tag{7}$$

$$|q_i\rangle = |q_i'\rangle \cos\theta_{ij} - |q_j'\rangle \sin\theta_{ij} \tag{8}$$

$$|q_j\rangle = |q_i'\rangle \sin\theta_{ij} + |q_j'\rangle \cos\theta_{ij} \tag{9}$$

which can be multiplied by the nonorthogonal counterparts with weights to obtain the weighted overlap sum for the pair, OVLPS_{ij}:

$$\begin{aligned} \text{OVLPS}_{ij} = {} & w_i \langle p_i | q_i' \rangle \cos\theta_{ij} - w_i \langle p_i | q_j' \rangle \sin\theta_{ij} \\ & + w_j \langle p_j | q_i' \rangle \sin\theta_{ij} + w_j \langle p_j | q_j' \rangle \cos\theta_{ij} \end{aligned} \tag{10}$$

Factoring by the trigonometric functions gives

$$\text{OVLPS}_{ij} = B_{ij}\cos\theta_{ij} + C_{ij}\sin\theta_{ij} \tag{11}$$

where

$$B_{ij} = w_i \left\langle p_i \middle| q_i' \right\rangle + w_j \left\langle p_j \middle| q_j' \right\rangle \tag{12}$$

$$C_{ij} = w_j \left\langle p_j \middle| q_i' \right\rangle - w_i \left\langle p_i \middle| q_j' \right\rangle \tag{13}$$

By using the trigonometric identity

$$\cos\left(\theta_{ij} - \gamma_{ij}\right) = \cos\theta_{ij}\cos\gamma_{ij} + \sin\theta_{ij}\sin\gamma_{ij} \tag{14}$$

the two terms in Equation (11) can be combined into one by multiplying Equation (14) with A_{ij} and comparing it:

$$\mathrm{OVLPS}_{ij} = A_{ij}\cos\left(\theta_{ij} - \gamma_{ij}\right) \tag{15}$$

where

$$\cos\gamma_{ij} = \frac{B_{ij}}{A_{ij}} \tag{16}$$

$$\sin\gamma_{ij} = \frac{C_{ij}}{A_{ij}} \tag{17}$$

$$A_{ij} = \sqrt{B_{ij}^2 + C_{ij}^2} \tag{18}$$

OVLPS_{ij} is maximized when $\theta_{ij} = \gamma_{ij}$ in Equation (15). $\cos\gamma_{ij}$ and $\sin\gamma_{ij}$ are used to construct the rotation matrix in Equation (7) to determine $\left|q_i\right\rangle$ and $\left|q_j\right\rangle$. Rotations occur in sweeps, where each sweep is a sequence of Equation (7) for all pairs of i and j, and the process repeats until convergence is attained[4,5].

Notes and references

1 C. Freysoldt, S. Boeck and J. Neugebauer, *Phys. Rev. B*, 2009, **79**, 241103.

2 N. Marzari, D. Vanderbilt and M. C. Payne, *Phys. Rev. Lett.*, 1997, **79**, 1337.

3 A. West, *Computational and Theoretical Chemistry*, 2014, **1045**, 73–77.

4 S. Rajasekaran and M. Song, *Journal of Parallel and Distributed Computing*, 2008, **68**, 769–777.

5 C. Sanderson and R. Curtin, *Journal of Open Source Software*, 2016, **1**, 26.