density matrix embedding theory SCF optimization

Abstract

I. INTRODUCTION

II. THEORY

DMET SCF

$$\Delta = ||\langle\Phi|a_r^\dagger a_s|\Phi\rangle - \langle\Psi_A|a_r^\dagger a_s|\Psi_A\rangle||^2 \tag{1}$$

For the given density matrix $\mathbf{D}^{ref}$ and Fock operator f^A, find a pseudo-potential $\tilde{u}$ that the associated density $\tilde{\mathbf{D}}$

$$(f^A + \tilde{u}) \rightarrow \tilde{\mathbf{D}} \tag{2}$$

minimize the distance to the referenced density matrix $\mathbf{D}^{ref}$

$$d = \sum_{rs\in A} ||\tilde{\mathbf{D}}_{rs}^{ref} - \mathbf{D}_{rs}||^2 \tag{3}$$

A. Fixed Fock operator

Fixed Fock operator means the Fock operator f^A is independent of density matrix. Starting from a initial guess u_0, the algorithm should find a solution sequence which converges to the desired pseudo-potential $\tilde{u}$

$$u_0, u_1, \cdots, u_k, \cdots, \tilde{u}$$

If u_k is the potential of kth iteration, the $k+1$th potential u_{k+1} are obtained as follows: Define the unperturbed and perturbed Fock operator

$$f^A + \tilde{u} = F^0 + F^1 \tag{4}$$

$$F^0 = f^A + u_k \tag{5}$$

$$F^1 = \mathcal{V} = \tilde{u} - u_k \tag{6}$$

Using perturbation technique to solve the eigenvalue problem

$$\mathbf{F}\mathbf{C} = \mathbf{C}E \tag{7}$$

The solution is

$$\mathbf{C}^1_{ij} = 0 \tag{8}$$

$$\mathbf{C}^1_{ai} = \frac{\mathcal{V}_{ai}}{E^0_i - E^0_a} = \frac{\mathbf{C}^{0*}_{ra}\mathcal{V}_{rs}\mathbf{C}^0_{si}}{E^0_i - E^0_a} \tag{9}$$

Let

$$\mathcal{E}_{rs,ai} = -\frac{\mathbf{C}^{0*}_{ra}\mathbf{C}^0_{si}}{E^0_a - E^0_i} = -\mathcal{E}^*_{sr,ia} \tag{10}$$

The first order solution turns to be

$$\mathbf{C}^1_{ai} = \mathcal{E}_{rs,ai}\mathcal{V}_{rs} \tag{11}$$

the first order density matrix is

$$\mathbf{D}^1_{pq} = \mathbf{C}^0_{pi}\mathbf{C}^{1*}_{qi} + \mathbf{C}^1_{pi}\mathbf{C}^{0*}_{qi} \tag{12}$$

$$\mathbf{D}^1_{ij} = 0 \tag{13}$$

$$\mathbf{D}^1_{ai} = \mathbf{C}^1_{ai} = \sum_{rs}\mathcal{E}_{rs,ai}\mathcal{V}_{rs} \tag{14}$$

$$\mathbf{D}^1_{ia} = \mathbf{C}^{1*}_{ai} = \sum_{rs}\mathcal{E}^*_{rs,ai}\mathcal{V}^*_{rs} = -\sum_{rs}\mathcal{E}_{sr,ia}\mathcal{V}_{sr} \tag{15}$$

$$\mathbf{D}^1_{ab} = 0 \tag{16}$$

Define the distance

$$\tilde{d} = ||\mathbf{D}^{ref}_{\in A} - \mathbf{D}^0_{\in A} - \mathbf{D}^1_{\in A}||^2 \tag{17}$$

$$= Tr[(\mathbf{D}^{ref}_{\in A} - \mathbf{D}^0_{\in A} - \mathbf{D}^1_{\in A})^\dagger(\mathbf{D}^{ref}_{\in A} - \mathbf{D}_{\in A} - \mathbf{D}^1_{\in A})] \tag{18}$$

$$= Tr(\mathbf{D}^{ref}_{\in A} - \mathbf{D}^0_{\in A} - \mathbf{D}^1_{\in A})^2 \tag{19}$$

where

$$\mathbf{D}^{ref}_{\in A,rs} = \mathbf{D}^{ref}_{rs}, \quad rs \in A \tag{20}$$

$$\mathbf{D}^0_{\in A,rs} = \mathbf{D}^0_{rs} \quad rs \in A \tag{21}$$

$$\mathbf{D}^1_{\in A,rs} = \sum_{ai}\mathbf{C}^0_{ra}(\mathcal{E}\mathcal{V})_{ai}\mathbf{C}^{0*}_{si} + \mathbf{C}^0_{ri}(\mathcal{E}\mathcal{V})^*_{ai}\mathbf{C}^{0*}_{sa} \tag{22}$$

So the first order derivative of d is

$$\frac{\partial d}{\partial \mathcal{V}_{tu}} = \sum_{rs} (\mathbf{D}^{ref}_{\in A,rs} - \mathbf{D}^{0}_{\in A,rs} - \mathbf{D}^{1}_{\in A,rs}) \frac{\partial \mathbf{D}^{1}_{\in A,sr}}{\partial \mathcal{V}_{tu}} = 0 \tag{23}$$

$$\mathbf{D}^{ref}_{\in A,ai} = \sum_{rs\in A} \mathbf{C}^{0*}_{ra} \mathbf{D}^{ref}_{rs} \mathbf{C}^{0}_{si} \tag{24}$$

$$\mathbf{D}^{0}_{\in A,ai} = \sum_{rs\in A} \mathbf{C}^{0*}_{ra} \mathbf{D}^{0}_{rs} \mathbf{C}^{0}_{si} \tag{25}$$

Using $\mathcal{V}_{tu} = \mathcal{V}^*_{ut}$,

$$\sum_{rs} (\mathbf{D}^{ref}_{\in A,rs} - \mathbf{D}^{0}_{\in A,rs}) \frac{\partial \mathbf{D}^{1}_{\in A,sr}}{\partial \mathcal{V}_{tu}} = G_{tu} + G^*_{ut} \tag{26}$$

$$\sum_{ai} (\mathbf{D}^{ref}_{\in A,ia} - \mathbf{D}^{0}_{\in A,ia}) \mathcal{E}_{tu,ai} = \sum_{ai} \frac{\mathbf{C}^{0}_{ui} (\mathbf{D}^{ref}_{\in A,ia} - \mathbf{D}^{0}_{\in A,ia}) \mathbf{C}^{0*}_{ta}}{E^0_i - E^0_a} = G_{tu} \tag{27}$$

$$\sum_{ai} (\mathbf{D}^{ref}_{\in A,ai} - \mathbf{D}^{0}_{\in A,ai}) \mathcal{E}^*_{ut,ai} = \sum_{ai} \frac{\mathbf{C}^{0}_{ua} (\mathbf{D}^{ref}_{\in A,ai} - \mathbf{D}^{0}_{\in A,ai}) \mathbf{C}^{0*}_{ti}}{E^0_i - E^0_a} = G^*_{ut} \tag{28}$$

$$\begin{aligned}
\sum_{rs} \mathbf{D}^{1}_{\in A,rs} \frac{\partial \mathbf{D}^{1}_{\in A,sr}}{\partial \mathcal{V}_{tu}} &= \sum_{abij,rs\in A} (\mathcal{E}\mathcal{V})_{ai} \mathbf{C}^{0*}_{si} \mathbf{C}^{0}_{sb} \mathcal{E}_{tu,bj} \mathbf{C}^{0*}_{rj} \mathbf{C}^{0}_{ra} + (\mathcal{E}\mathcal{V})_{ai} \mathbf{C}^{0*}_{si} \mathbf{C}^{0}_{sj} \mathcal{E}^*_{ut,bj} \mathbf{C}^{0*}_{rb} \mathbf{C}^{0}_{ra} \\
&\quad + (\mathcal{E}\mathcal{V})^*_{ai} \mathbf{C}^{0*}_{sa} \mathbf{C}^{0}_{sj} \mathcal{E}^*_{ut,bj} \mathbf{C}^{0*}_{rb} \mathbf{C}^{0}_{ri} + (\mathcal{E}\mathcal{V})^*_{ai} \mathbf{C}^{0*}_{sa} \mathbf{C}^{0}_{sb} \mathcal{E}_{tu,bj} \mathbf{C}^{0*}_{rj} \mathbf{C}^{0}_{ri} \\
&= \sum_{vw} H_{tu,vw} \mathcal{V}_{vw}
\end{aligned} \tag{29}$$

where

$$\begin{aligned}
H_{tu,vw} = &\sum_{abij,rs\in A} \mathcal{E}_{vw,ai} \mathbf{S}_{\in A,ib} \mathcal{E}_{tu,bj} \mathbf{S}_{\in A,ja} + \mathcal{E}_{vw,ai} \mathbf{S}_{\in A,ij} \mathcal{E}^*_{ut,bj} \mathbf{S}_{\in A,ba} \\
&+ \mathcal{E}^*_{wv,ai} \mathbf{S}_{\in A,aj} \mathcal{E}^*_{ut,bj} \mathbf{S}_{\in A,bi} + \mathcal{E}^*_{wv,ai} \mathbf{S}_{\in A,ab} \mathcal{E}_{tu,bj} \mathbf{S}_{\in A,ij}
\end{aligned} \tag{30}$$

$$\mathbf{S}_{\in A,pq} = \sum_{r\in A} \mathbf{C}^{0*}_{rp} \mathbf{C}^{0}_{rq} \tag{31}$$

Eq. (23) turns to be a linear equation

$$H\mathcal{V} = (G + G^\dagger) \tag{32}$$

To avoid singularity in H, small number is added to the diagonal elements

$$(H + \delta)\mathcal{V} = (G + G^\dagger) + (u_k - u_{k-1})\delta \tag{33}$$

It can damp the results. When the sequence $u_1, u_2, \ldots$ is converged,

$$u_k - u_{k-1} = u_{k+1} - u_k = \mathcal{V} \to 0 \tag{34}$$

The damped equation (33) will turn to be the original one (32).

B. Relaxed Fock operator

Relaxed Fock operator means the Fock operator depends on the density matrix $f^A(\mathbf{D})$.

$$V^{HF}_{pq} = V^{HF0}_{pq} + V^{HF1}_{pq} = V^{HF0}_{pq} + \sum_{rs}(pq||rs)\mathbf{D}^1_{sr} = V^{HF0}_{pq} + \sum_{rs}(pq|rs)\mathbf{D}^1_{sr} - \sum_{rs}(ps|rq)\mathbf{D}^1_{sr} \tag{35}$$

So we have coupled equations

$$\begin{cases} \mathbf{D}^1 = \mathcal{E}F^1 \\ F^1_{pq} = \bar{\mathcal{V}}_{pq} + \sum_{rs}(pq||rs)\mathbf{D}^1_{sr} \end{cases} \tag{36}$$

$$\bar{\mathcal{V}} = F^1 - (pq||rs)\mathcal{E}F^1 \tag{37}$$

$$\bar{\mathcal{V}}_{rs} = \bar{F}^1_{rs} - \sum_{ia}(rs||ia)\mathbf{D}^1_{ai} - \sum_{ia}(rs||ai)\mathbf{D}^1_{ia} \tag{38}$$

$$= \left(\delta_{rs,tu} - \sum_{iatu}[(rs|ia) - (ra|is)]\mathcal{E}_{tu,ai} - \sum_{iatu}[(rs|ai) - (ri|as)]\mathcal{E}^*_{ut,ai}\right)\bar{F}^1_{tu} \tag{39}$$

For closed-shell system

$$\bar{\mathcal{V}}_{rs} = \left(\delta_{rs,tu} - \sum_{iatu}[2(rs|ia) - (ra|is)]\mathcal{E}_{tu,ai} - \sum_{iatu}[2(rs|ai) - (ri|as)]\mathcal{E}^*_{ut,ai}\right)\bar{F}^1_{tu} \tag{40}$$

After solving Eq. (32) to obtain $\bar{F}^1$, the solution of linear Eq. (39) gives the one-electron pseudo potential which minimizes d for the relaxed Fock operator $f^A(\mathbf{D})$.

C. Fitting the density matrix diagonal terms

Fit the diagonal term of fitting potential to optimize the diagonal term of the mean field density matrix. The distance is defined on the diagonal terms of density matrix

$$\tilde{d} = \sum_{r\in A} ||\mathbf{D}^{ref}_{rr} - \mathbf{D}^0_{rr} - \mathbf{D}^1_{rr}||^2 \tag{41}$$

So the first order derivative of d is

$$\frac{\partial d}{\partial \mathcal{V}_{tt}} = \sum_{r\in A}(\mathbf{D}^{ref}_{rr} - \mathbf{D}^0_{rr} - \mathbf{D}^1_{rr})\frac{\partial \mathbf{D}^1_{rr}}{\partial \mathcal{V}_{tt}} = 0 \tag{42}$$

$$\sum_{r}(\mathbf{D}^{ref}_{rr} - \mathbf{D}^0_{rr})\frac{\partial \mathbf{D}^1_{rr}}{\partial \mathcal{V}_{tu}} = G_{tt} + G^*_{tt} \tag{43}$$

$$G_{tt} = \sum_{ai,r\in A} (\mathbf{D}^{ref}_{rr} - \mathbf{D}^{0}_{rr})\mathbf{C}^{0}_{ra}\mathcal{E}_{tt,ai}\mathbf{C}^{0*}_{ri} = \sum_{r\in A}(\mathbf{D}^{ref}_{rr} - \mathbf{D}^{0}_{rr})\mathcal{X}_{tr} \tag{44}$$

$$G^{*}_{tt} = \sum_{ai,r\in A} (\mathbf{D}^{ref}_{rr} - \mathbf{D}^{0}_{rr})\mathbf{C}^{0}_{ri}\mathcal{E}^{*}_{tt,ai}\mathbf{C}^{0*}_{ra} = \sum_{r\in A}(\mathbf{D}^{ref}_{rr} - \mathbf{D}^{0}_{rr})\mathcal{W}_{tr} \tag{45}$$

$$\mathcal{X}_{tr} = \sum_{ai} \mathbf{C}^{0}_{ra}\mathcal{E}_{tt,ai}\mathbf{C}^{0*}_{ri} \tag{46}$$

$$\mathcal{W}_{tr} = \sum_{ai} \mathbf{C}^{0}_{ri}\mathcal{E}^{*}_{tt,ai}\mathbf{C}^{0*}_{ra} = \mathcal{X}^{*}_{tr} \tag{47}$$

$$\begin{aligned}
\sum_{r\in A}\mathbf{D}^{1}_{rr}\frac{\partial \mathbf{D}^{1}_{rr}}{\partial \mathcal{V}_{tt}} &= \sum_{abij,r\in A} (\mathcal{E}\mathcal{V})_{ai}\mathbf{C}^{0*}_{ri}\mathbf{C}^{0}_{rb}\mathcal{E}_{tt,bj}\mathbf{C}^{0*}_{rj}\mathbf{C}^{0}_{ra} + (\mathcal{E}\mathcal{V})_{ai}\mathbf{C}^{0*}_{ri}\mathbf{C}^{0}_{rj}\mathcal{E}^{*}_{tt,bj}\mathbf{C}^{0*}_{rb}\mathbf{C}^{0}_{ra} \\
&+ (\mathcal{E}\mathcal{V})^{*}_{ai}\mathbf{C}^{0*}_{ra}\mathbf{C}^{0}_{rj}\mathcal{E}^{*}_{tt,bj}\mathbf{C}^{0*}_{rb}\mathbf{C}^{0}_{ri} + (\mathcal{E}\mathcal{V})^{*}_{ai}\mathbf{C}^{0*}_{ra}\mathbf{C}^{0}_{rb}\mathcal{E}_{tt,bj}\mathbf{C}^{0*}_{rj}\mathbf{C}^{0}_{ri} \\
&= \sum_{u} H_{tu}\mathcal{V}_{uu}
\end{aligned} \tag{48}$$

where

$$\begin{aligned}
H_{tu} &= \sum_{r\in A} \mathcal{X}_{tr}\mathcal{X}_{ur} + \mathcal{X}^{*}_{tr}\mathcal{X}_{ur} + \mathcal{X}^{*}_{tr}\mathcal{X}^{*}_{ur} + \mathcal{X}_{tr}\mathcal{X}^{*}_{ur} \\
&= \sum_{r\in A} \mathcal{X}_{tr}\mathcal{X}_{ur} + \mathcal{W}_{tr}\mathcal{X}_{ur} + \mathcal{W}_{tr}\mathcal{W}_{ur} + \mathcal{X}_{tr}\mathcal{W}_{ur} \\
&= \sum_{r\in A}(\mathcal{X}_{tr} + \mathcal{W}_{tr})(\mathcal{X}_{ur} + \mathcal{W}_{ur})
\end{aligned} \tag{49}$$

The linear equation is

$$H\mathcal{V} = (G + G^{\dagger}) \tag{50}$$