Density Matrix Minimization: Non-orthogonal Basis

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[R.W. Nunes & D. Vanderbilt, PRB 50, 17611 ('94)]

- Non-orthogonal basis

[E.B. Stechel, A.R. Williams, P.J. Feibelman, PRB 49, 10088 ('94)]

Consider a non-orthogonal basis set $\{|i\rangle \mid i=1,\ldots,M\}$. Let the overlap matrix be

$$S_{ij} = \langle i|j\rangle \tag{1}$$

Note that $S \in \mathbb{R}^{M\times M}$ is unitary

$$S^{\dagger} = S \tag{2}$$

$\because (S^{\dagger})_{ij} = (S_{ji})^* = (\langle j|i\rangle)^* = \langle i|j\rangle = S_{ij}$ //

(Restriction)

1. We consider a case where S is not singular, i.e., rank $S = M$ and $|i\rangle$'s are linearly independent. Ill-defined (redundancy ill-definition) and singular S will be considered in a separate note.

2. We work in the vector space, span$\{|i\rangle\}$, so that the basis set can be considered complete.

(Biorthogonal complement)

We define the bi-orthogonal complement set $\{|\bar{i}\rangle\}$ as

$$|\bar{i}\rangle = \sum_j |j\rangle S^{-1}_{ji} \tag{3}$$

(※ Note this requires invertable S, while overlapping divide-&-conquer may have linearly less-independent orbitals.)

(Theorem: biorthogonality)

$$\langle \bar{i}|j\rangle = \langle i|\bar{j}\rangle = \delta_{ij} \tag{4}$$

∵ $\langle \bar{i}|j\rangle = \sum_k \underbrace{(S^{-1})^{+}_{ik}}_{(S^{-1})_{ik}\ (\because \text{unitary})} \underbrace{\langle k|j\rangle}_{S_{kj}} = \delta_{ij}$

$\langle i|\bar{j}\rangle = \langle i|\sum_k |k\rangle S^{-1}_{kj} = \sum_k S_{ik} S^{-1}_{kj} = \delta_{ij}$ //

(Theorem: closure relation)

$$I = \sum_i |\bar{i}\rangle\langle i| = \sum_i |i\rangle\langle \bar{i}| = \sum_{ij} |i\rangle S^{-1}_{ij} \langle j| \tag{5}$$

∵ We work in the vector space, where $\{|i\rangle\}$ is complete, any vector $|v\rangle$ can be represented a linear combination of $|i\rangle$'s.

$$|v\rangle = \sum_j C_j |j\rangle$$

To determine C_i, $\langle \bar{i}| \times$ above

$$\langle \bar{i}|v\rangle = \sum_j C_j \underbrace{\langle \bar{i}|j\rangle}_{\delta_{ij}} = C_i$$

$$\therefore |{}^{\forall}v\rangle = \sum_j |j\rangle\langle \bar{j}|v$$

Therefore,

$$I = \sum_i |i\rangle\langle\bar{i}|$$

$$= \sum_i \sum_j |i\rangle S^{-1}_{ij} \langle j|$$

$$= \sum_j \underbrace{\left(\sum_i |i\rangle S^{-1}_{ij}\right)}_{|\bar{j}\rangle} \langle j|$$

$$= \sum_j |\bar{j}\rangle\langle j| \quad //$$

– Generalized eigenvalue problem

Consider the energy eigenstates

$$\begin{cases} \hat{H}|n\rangle = \varepsilon_n |n\rangle & (6) \\ \langle n|n'\rangle = \delta_{nn'} \quad \text{(orthogonality)} & (7) \end{cases}$$

Let's represent Eq.(6) in the non-orthogonal basis. Note

$$|n\rangle = \sum_i |i\rangle\langle\tilde{i}|n\rangle$$

$$= \sum_{ij} |i\rangle S^{-1}_{ij} \langle j|n\rangle$$

$$= \sum_i |i\rangle \underbrace{\left(\sum_j S^{-1}_{ij} \langle j|n\rangle\right)}_{C_{in}}$$

$$\therefore |n\rangle = \sum_i |i\rangle C_{in} \qquad (8)$$

$$C_{in} = \sum_j S^{-1}_{ij} \langle j|n\rangle \qquad (9)$$

Substituting Eq.(9) in (6) and $\langle i| \times$ Eq.(6),

$$\langle i|\hat{H}\sum_j |j\rangle C_{jn} = \langle i|n\rangle \varepsilon_n \qquad (10)$$

Note that, by $\sum_i S_{ji} \times$ Eq.(9)

$$\sum_i S_{ji} C_{in} = \sum_{ij'} S_{ji} S^{-1}_{ij'} \langle j'|n\rangle$$

$$= \sum_{j'} \underbrace{\left(\sum_i S_{ji} S^{-1}_{ij'}\right)}_{\delta_{jj'}} \langle j'|n\rangle = \langle j|n\rangle$$

$$\therefore \langle i|n\rangle = \sum_j S_{ij} C_{jn} \qquad (11)$$

Substituting Eq. (11) in (10)

$$\sum_j \langle i|\hat{H}|j\rangle C_{jn} = \sum_j S_{ij} C_{jn} \epsilon_n$$

$$HC = SC\Lambda \tag{12}$$

where

$$\begin{cases} H_{ij} = \langle i|\hat{H}|j\rangle & (13) \\ C_{in} = \sum_j S^{-1}_{ij} \langle j|n\rangle \quad \left(\text{or } |n\rangle = \sum_i |i\rangle C_{in} \right) & (14) \\ S_{ij} = \langle i|j\rangle & (15) \\ \Lambda = \mathrm{diag}(\epsilon_1, \epsilon_2, \ldots, \epsilon_M) & (16) \end{cases}$$

(Orthogonality)

Substitute the expansion (8) in Eq. (7)

$$\sum_i C^*_{ni} \langle i| \sum_j |j\rangle C_{jn'} = \delta_{nn'}$$

$$\sum_{ij} \underbrace{C^*_{ni}}_{C^{\dagger}_{ni}} \underbrace{\langle i|j\rangle}_{S_{ij}} \underbrace{C_{jn'}}_{C_{jn'}} = \delta_{nn'}$$

$$\therefore\ C^{\dagger}SC = I \tag{17}$$

$C \times$ Eq. (17)

$$\underbrace{(CC^{\dagger})SC}_{I} = C$$

$$\therefore\ CC^{\dagger} = S^{-1}$$

Eq. (17) $\times\ C^{\dagger}$

$$C^{\dagger}\underbrace{S(CC^{\dagger})}_{I} = C^{\dagger}$$

$$\therefore\ CC^{\dagger} = S^{-1}$$

Therefore,

$$CC^{\dagger} = S^{-1} \tag{18}$$

(Another path)

$$\sum_n C_{in} C^{\dagger}_{nj} = \sum_n \sum_{i'j'} S^{-1}_{ii'} \underbrace{\langle i'|n\rangle\langle n|j'\rangle}_{\langle i'|j'\rangle = S_{i'j'}} S^{-1}_{j'j} = \sum_{i'j'} \underbrace{S^{-1}_{ii'} S_{i'j'}}_{\delta_{ij'}} S^{-1}_{j'j} = S^{-1}_{ij} \quad //$$

(Spectral decomposition)

$$H_{ij} = \langle i | \sum_m |m\rangle\langle m| \hat{H} \sum_n |n\rangle\langle n | j\rangle$$

$$= \sum_{mn} \langle i | m\rangle \underbrace{\langle m|\hat{H}|n\rangle}_{\epsilon_m \delta_{mn} = \Lambda_{mn}} \langle n | j\rangle$$

$$= \sum_{mn} \sum_{i'j'} S_{ii'} C_{i'm} \Lambda_{mn} C^*_{nj'} S_{j'j}$$

$$= (SC\Lambda C^\dagger S)_{ij}$$

$$\therefore \; H = SC\Lambda C^\dagger S \tag{19}$$

$C^\dagger \times$ Eq.(19) $\times$ C

$$C^\dagger H C = \underbrace{C^\dagger S C}_{I} \Lambda \underbrace{C^\dagger S C}_{I}$$

$$\therefore \; C^\dagger H C = \Lambda \tag{20}$$

– Density matrix

$$\hat{\rho}_{gs} = \Theta(\mu - \hat{H}) \tag{21}$$

The ground-state density matrix is idempotent (see 6/18/03),

$$\hat{\rho}_{gs}^{\,2} = \hat{\rho}_{gs} \tag{22}$$

Within the non-orthogonal basis

$$\langle i|\hat{\rho}_{gs}\underbrace{\,}_{\sum_{i'j'}|i'\rangle S^{-1}_{i'j'}\langle j'|}\hat{\rho}_{gs}|j\rangle = \langle i|\hat{\rho}_{gs}|j\rangle$$

(∵ closure relation (5))

$$\sum_{i'j'}\langle i|\hat{\rho}_{gs}|i'\rangle S^{-1}_{i'j'}\langle j'|\hat{\rho}_{gs}|j\rangle = \langle i|\hat{\rho}_{gs}|j\rangle$$

$$\therefore \quad \rho_{gs} S^{-1} \rho_{gs} = \rho_{gs} \tag{23}$$

where

$$(\rho_{gs})_{ij} = \langle i|\hat{\rho}_{gs}|j\rangle \tag{24}$$

In the following variational calculation, we impose the idempotency to the trial ρ

$$\therefore \quad \rho S^{-1} \rho = \rho \tag{25}$$

where

$$\rho_{ij} = \langle i|\hat{\rho}|j\rangle \tag{26}$$

– Grand potential

The number of electrons N_e is given by

$$N_e = \sum_n \Theta(\mu - \hat{H})$$

$$= \sum_n \langle n | \Theta(\mu - \hat{H}) | n \rangle$$

Using Eq. (8),

$$N_e = \sum_n \sum_{ij} \underbrace{C^*_{in}}_{C^+_{ni}} \langle i | \Theta(\mu - \hat{H}) | j \rangle C_{jn}$$

$$= \sum_{ij} \underbrace{\langle i | \Theta(\mu - \hat{H}) | j \rangle}_{(\rho_{gs})_{ij}} \underbrace{\sum_n C_{jn} C^+_{ni}}_{S^{-1}_{ji}}$$

$$\therefore N_e = \sum_{ij} (\rho_{gs})_{ij} S^{-1}_{ji} = tr(\rho_{gs} S^{-1}) \qquad (27)$$

We generalize this normalization to general trial $\hat{\rho}$.

$$N_e = tr(\rho S^{-1}) \qquad (28)$$

The ground-state energy is

$$E_{gs} = \sum_n \Theta(\mu - \epsilon_n) \epsilon_n$$

$$= \sum_n \langle n | \hat{\rho}_{gs} \underbrace{\,}_{\sum_{ij} |i\rangle S^{-1}_{ij} \langle j|} \hat{H} | n \rangle$$

$$= \sum_n \sum_{ij} \langle n | \hat{\rho}_{gs} | i \rangle S^{-1}_{ij} \langle j | \hat{H} | n \rangle$$

$$= \sum_{ij} \langle j | \hat{H} \underbrace{\,}_{\sum_{i'j'} |i'\rangle S^{-1}_{i'j'} \langle j'|} \hat{\rho}_{gs} | i \rangle S^{-1}_{ij} \qquad (\because \sum_n |n\rangle\langle n| = I)$$

$$= \sum_{ij} \sum_{i'j'} \underline{\langle j | \hat{H} | i' \rangle} S^{-1}_{i'j'} \underline{\langle j' | \hat{\rho}_{gs} | i \rangle} S^{-1}_{ij}$$

$$\therefore E_{gs} = \sum_j (H S^{-1} \rho_{gs} S^{-1})_{jj} = tr(\rho_{gs} S^{-1} H S^{-1}) \quad (29)$$

We generalize this to general variational function $\hat{\rho}$

$$E[\rho] = tr(\rho S^{-1} H S^{-1}) \quad (30)$$

The grand potential is

$$\Omega = E[\rho] - \mu N_e$$

$$= tr\left[\rho\,(S^{-1} H S^{-1} - \mu S^{-1})\right] \quad (31)$$

— Modified grand potential

The purified trial density matrix $\hat{\tilde{\rho}}$ is defined as

$$\hat{\tilde{\rho}} = 3\hat{\rho}^2 - 2\hat{\rho}^3 \tag{32}$$

In the non-orthogonal representation,

$$\langle i|\hat{\tilde{\rho}}|j\rangle = 3\langle i|\hat{\rho}\hat{\rho}|j\rangle - 2\langle i|\hat{\rho}\hat{\rho}\hat{\rho}|j\rangle$$

$$\sum_{i'j'}|i'\rangle S^{-1}_{i'j'}\langle j'| \qquad \sum_{i'j'}|i'\rangle S^{-1}_{i'j'}\langle j'| \qquad \sum_{i''j''}|i''\rangle S^{-1}_{i''j''}\langle j''|$$

$$= 3(\rho S^{-1}\rho)_{ij} - 2(\rho S^{-1}\rho S^{-1}\rho)_{ij}$$

$$\therefore\ \tilde{\rho} = 3\rho S^{-1}\rho - 2\rho S^{-1}\rho S^{-1}\rho \tag{33}$$

With the purified density matrix, the modified grand potential (to be minimized without idempotency constraint) is

$$\Omega' = \mathrm{tr}[\tilde{\rho}(S^{-1}HS^{-1} - \mu S^{-1})] \tag{34}$$

$$= \mathrm{tr}[(3\rho S^{-1}\rho - 2\rho S^{-1}\rho S^{-1}\rho)(S^{-1}HS^{-1} - \mu S^{-1})] \tag{35}$$

– Change of variables

Let's define

$$\bar{\rho} = S^{-1} \rho S^{-1} \tag{36}$$

or

$$\rho = S \bar{\rho} S \tag{37}$$

Substituting Eq. (37) in (35),

$$\Omega'[\bar{\rho}] = tr\left[\left(3S\bar{\rho}\cancel{S S^{-1}}S\bar{\rho}S - 2S\bar{\rho}\cancel{S S^{-1}}S\bar{\rho}\cancel{S S^{-1}}S\bar{\rho}S\right)\left(S^{-1}HS^{-1} - \mu S^{-1}\right)\right]$$

$$= tr\left[S\left(3\bar{\rho}S\bar{\rho} - 2\bar{\rho}S\bar{\rho}S\bar{\rho}\right)S\left(S^{-1}HS^{-1} - \mu S^{-1}\right)\right]$$

$$= tr\left[\left(3\bar{\rho}S\bar{\rho} - 2\bar{\rho}S\bar{\rho}S\bar{\rho}\right)\underbrace{S\left(S^{-1}HS^{-1} - \mu S^{-1}\right)S}_{H - \mu S}\right]$$

Unconditionally minimize

$$\Omega'[\bar{\rho}] = tr\left[\left(3\bar{\rho}S\bar{\rho} - 2\bar{\rho}S\bar{\rho}S\bar{\rho}\right)\left(H - \mu S\right)\right] \tag{38}$$

The physical density matrix is obtained from the optimal $\bar{\rho}$ as

$$\rho = S\bar{\rho}S \tag{39}$$