Density Matrix Minimization: Orthogonal Basis

[X.-P. Li, R.W. Nunes, D. Vanderbilt, PRB 47, 10891 (1993)]

Density matrix

Let \( |n\rangle \) be the eigenstates of the Hamiltonian,

\[
\hat{H} |n\rangle = \varepsilon_n |n\rangle
\]

Then the density matrix is defined as

\[
\hat{\rho} = \sum_n |n\rangle \langle \mu | \Theta(\mu - \varepsilon_n) |n\rangle
\]

(Idempotency: projection operator)

\[
\hat{\rho}^2 = \sum_{m,n} |m\rangle \langle \mu | \Theta(\mu - \varepsilon_m) |m\rangle \langle m | \Theta(\mu - \varepsilon_n) |n\rangle \\
= \sum_{m,n} |m\rangle \Theta(\mu - \varepsilon_m) \langle m | \Theta(\mu - \varepsilon_n) |n\rangle \\
= \sum_n \langle n | \Theta^2(\mu - \varepsilon_n) |n\rangle = \hat{\rho} \\
= \Theta(\mu - \varepsilon_n)
\]

\[
\therefore \hat{\rho}^2 = \hat{\rho}
\]

(Normalization)

\[
\text{Tr} \hat{\rho} = \sum_n \langle n | \hat{\rho} |n\rangle \\
= \sum_{n,m} \langle m | \Theta(\mu - \varepsilon_m) \langle m | \Theta(\mu - \varepsilon_n) |n\rangle \\
= \sum_n \Theta(\mu - \varepsilon_n) = N_e
\]

\[
\therefore \text{Tr} \hat{\rho} = \sum_n \Theta(\mu - \varepsilon_n) = N_e
\]

where \( N_e \) is the number of electrons and \( \mu \) is the chemical potential.

(Hermiticity)

\[
\hat{\rho}^\dagger = \hat{\rho}
\]
(Positive definiteness)
All eigenvalues of $\hat{\rho}$ are 1 or 0; $\hat{\rho}$ is positive definite.

- Orthogonal representation
Let $\{ |i\> | i = 1, \ldots, NM \}$ be an orthonormal basis, $\langle ii'\rangle = \delta_{ii'}$, attached to atoms, where $N$ is the number of atoms and $M$ is the number of basis orbitals per atom.

$$
\rho_{ij} = \langle ii'\hat{\rho}jj'\rangle \\
= \sum_n \langle ii'n\rangle \Theta(\mu - \varepsilon_n) \langle njj'\rangle \\
= \sum_n \psi_{ni} \Theta(\mu - \varepsilon_n) \psi_{jn}^* \\
(6)
$$

- Grand-canonical energy: constrained minimization
$$
\Omega = \text{tr}[\hat{\rho}(\hat{H} - \mu)] \\
= \sum_{ij} \rho_{ij} (H_{ij} - \mu \delta_{ij}) \\
(7)
$$
The ground state is obtained by minimizing Eq. (7) with the idempotency constraint, Eq. (3), for a given $\mu$. The number of electrons for this ground state is then obtained from Eq. (4).
Unconstrained minimization

Let us defined a purified version of a trial density matrix, $\tilde{\rho}$, as

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

(9)

The modified grand potential is then defined as

$$\tilde{\Omega} = tr[\tilde{\rho}(\hat{H} - \mu)]$$

(10)

$$= tr[(3\hat{\rho}^2 - 2\hat{\rho}^3)(\hat{H} - \mu)]$$

(11)

$$= tr[(3\hat{\rho}^2 - 2\hat{\rho}^3)\hat{H}']$$

(12)

where

$$\hat{H}' = \hat{H} - \mu$$

(13)

(Gradient)

$$\delta \tilde{\Omega} = tr[3(\hat{\rho}\delta \hat{\rho} + \delta \hat{\rho}\hat{\rho})\hat{H}' - 2(\hat{\rho}^2\delta \hat{\rho} + \delta \hat{\rho}\hat{\rho} + \hat{\rho}\delta \hat{\rho})\hat{H}']$$

(14)

$$(\text{cyclic shifts})$$

Note that the gradient is defined as

$$\delta \tilde{\Omega} = tr(\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}} \delta \hat{\rho}) = \sum_{ij} (\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}})_{ij} \delta \rho_{ij}$$

(15)

Comparing Eqs. (14) and (15),

$$\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}} = 3(\hat{H}'\hat{\rho} + \hat{\rho}\hat{H}') - 2(\hat{\rho}^2\hat{H}' + \hat{\rho}\hat{H}'\hat{\rho} + \hat{\rho}\hat{H}'')$$

(16)
(Theorem) The unconstrained minimum of $\tilde{\mathcal{Z}}$ gives the constrained ground state of $\tilde{\mathcal{Z}}$.

\( \odot \) (Stationarity)

At the constrained minimum, $\hat{\rho}$ satisfies the idempotency condition, $\hat{\rho}^2 = \hat{\rho}$, and also $\hat{\rho} = \Theta(-\hat{H}')$ commutes with $\hat{H}'$.

Therefore,

$$\frac{\partial \tilde{\mathcal{Z}}}{\partial \hat{\rho}} = \hat{\rho} \hat{H}' - \hat{\rho}^2 \hat{H}' = 0$$

\( \odot \) (Minimum)

Let the trial $\hat{\rho}$ be expanded with the energy eigenstates,

$$\hat{\rho} = \sum_n |\psi_n \rangle \langle \psi_n|$$  \hspace{1cm} (18)

Within this variational space (which contains the ground state),

$$\tilde{\mathcal{Z}} = \sum_n (\epsilon_n - \mu) (3\omega_n^2 - 2\omega_n^3)$$  \hspace{1cm} (18)

The minimum of this function is $\omega$

$$\omega_n = \begin{cases} 1 & (\forall \epsilon_n < \mu) \\ 0 & (\forall \epsilon_n > \mu) \end{cases}$$

which is a minimum, with the correct ground-state value,

$$\mathcal{Z}_{\text{gs}} = \sum (\epsilon_n - \mu) \Theta(\mu - \epsilon_n)$$  \hspace{1cm} (19)
(single minimum)
Since $\tilde{g}$ is a cubic function of $\hat{p}$, along any line-minimization direction, there can be only one minimum.

(run-away solution)
There are run-away solutions, such as
$$\omega_n = \begin{cases} +\infty & (\forall \epsilon_n < \mu) \\ -\infty & (\forall \epsilon_n > \mu) \end{cases}$$
in the variational space (17), because of the cubic polynomial.
Localization algorithm

With exponential accuracy, \( P_{ij} \) can be approximated as

\[
P_{ij} = 0 \quad (\forall R_{ij} > R_c)
\]

where \( R_{ij} \) is the distance between atoms the basis orbitals \( i \) and \( j \) belong to, and \( R_c \) is the cut-off length.

Minimize

\[
\tilde{\Omega} = tr\left[ (\hat{\rho}^2 - 2\hat{\rho}^3)(\hat{\mathbf{N}} - \mathbf{1}) \right]
\]

with respect to \( P_{ij} \) with constraint

\[
P_{ij} = 0 \quad (\forall R_{ij} > R_c)
\]

using the conjugate gradient algorithm with gradient

\[
\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}} = 3(\hat{\mathbf{N}}\hat{\hat{\rho}} + \hat{\rho}\hat{\mathbf{N}}) - 2(\hat{\hat{\rho}}\hat{\rho}^2 + \hat{\rho}\hat{\hat{\rho}}\rho + \hat{\rho}^2\hat{\mathbf{N}})
\]
- On the constrained minimization, Eq.(x)

Minimize, with respect to $\hat{\rho}$,

$$\Omega = \text{tr} [ \hat{\rho} (\hat{H} - \mu) ]$$

with idempotency constraint

$$\hat{\rho}^2 - \hat{\rho} = 0$$

(24)

(25)

To solve this problem, we introduce Lagrange multipliers

$$\Omega' = \text{tr} [ \hat{\rho} (\hat{H} - \mu) - \hat{\Lambda} (\hat{\rho}^2 - \hat{\rho}) ]$$

(26)

The solution is stationary with respect to both $\hat{\rho}$ and $\hat{\Lambda}$,

$$\frac{\partial \Omega'}{\partial \hat{\Lambda}} = \hat{\rho}^2 - \hat{\rho} = 0$$

(27)

Functional derivative with respect to $\hat{\rho}$ is

$$\delta \Omega' = \text{tr} [(\hat{H} - \mu) \delta \hat{\rho} - \hat{\Lambda} (\delta \hat{\rho} + \delta \hat{\rho}^2 - \delta \hat{\rho})]$$

$$= \text{tr} [(\hat{H} - \mu) \delta \hat{\rho} - (\hat{\Lambda} \delta \hat{\rho} + \delta \hat{\rho} \hat{\Lambda} - \hat{\Lambda} \delta \hat{\rho})]$$

$$\therefore \frac{\partial \Omega'}{\partial \hat{\rho}} = \hat{H} - \mu - (\hat{\Lambda} \delta \hat{\rho} + \delta \hat{\rho} \hat{\Lambda} - \hat{\Lambda} \delta \hat{\rho}) = 0$$

(28)

Let's examine the solution in terms of the eigenstates of $\hat{\rho}$,

$$<m| \times \text{Eq. (27)} \times |n>$$

$$\rho_n^2 - \rho_n = \rho_n (\rho_n - 1) = 0$$

$$\therefore \rho_n = 1 \text{ or } 0$$

$$<m| \times \text{Eq. (27)} \times |n>$$

$$H_{mn} - \mu = \Lambda_{mn} (2\rho_n - 1)$$

$$\therefore \Lambda_{mn} = \begin{cases} H_{mn} - \mu & (\rho_n = 1) \\ \mu - H_{mn} & (\rho_n = 0) \end{cases}$$
McWeeny "purification" fixed-point iteration

\[ y = 3x^2 - 2x^3 \]