Density Matrix Minimization: Orthogonal Basis

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[X.-P. Li, R.W. Nunes, D. Vanderbilt, PRB 47, 10891 ('93)]

— Density matrix.

Let $|n\rangle$ be the eigenstates of the Hamiltonian,

$$\hat{H}\,|n\rangle = \varepsilon_n |n\rangle \tag{1}$$

Then the density matrix is defined as

$$\hat{\rho} = \sum_n |n\rangle \Theta(\mu-\varepsilon_n) \langle n| \tag{2}$$

(Idempotency: projection operator)

$$\hat{\rho}^2 = \sum_m |m\rangle \Theta(\mu-\varepsilon_m) \langle m| \sum_n |n\rangle \Theta(\mu-\varepsilon_n) \langle n|$$

$$= \sum_{m,n} |m\rangle \Theta(\mu-\varepsilon_m) \underbrace{\langle m|n\rangle}_{\delta_{mn}} \Theta(\mu-\varepsilon_n) \langle n|$$

$$= \sum_n |n\rangle \underbrace{\Theta^2(\mu-\varepsilon_n)}_{=\Theta(\mu-\varepsilon_n)} \langle n| = \hat{\rho}$$

$$\therefore\ \hat{\rho}^2 = \hat{\rho} \tag{3}$$

(Normalization)

$$\mathrm{Tr}\,\hat{\rho} = \sum_n \langle n|\hat{\rho}|n\rangle$$

$$= \sum_n \sum_m \underbrace{\langle n|m\rangle}_{\delta_{nm}} \Theta(\mu-\varepsilon_m) \underbrace{\langle m|n\rangle}_{\delta_{mn}}$$

$$= \sum_n \Theta(\mu-\varepsilon_n) = N_e$$

$$\therefore\ \mathrm{Tr}\,\hat{\rho} = \sum_n \Theta(\mu-\varepsilon_n) = N_e \tag{4}$$

where N_e is the number of electrons and μ is the chemical potential.

(Hermicity)

$$\hat{\rho}^\dagger = \hat{\rho} \tag{5}$$

(Postive definiteness)

All eigenvalues of $\hat{\rho}$ are 1 or 0; $\hat{\rho}$ is positive definite.

— Orthogonal representation

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

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

$$= \sum_n \underbrace{\langle i|n\rangle}_{\psi_{n,i}} \Theta(\mu-\varepsilon_n) \underbrace{\langle n|j\rangle}_{\psi^*_{j,n}}$$

$$= \sum_n \psi_{n,i}\Theta(\mu-\varepsilon_n)\psi^*_{j,n} \qquad (6)$$

— Grand-canonical energy: constrained minimization

$$\Omega = \mathrm{tr}[\hat{\rho}(\hat{H}-\mu)] \qquad (7)$$

$$= \sum_{i,j} \rho_{ij}(H_{ji} - \mu\delta_{ji}) \qquad (8)$$

The ground state is obtained by minimizing Eq. (7) with the idempotency constraint, Eq. (3), for a given μ. The number of electrons for this ground state is then obtained from Eq. (4).

– Unconstrained minimization

Let's defined a purified version of a trial density matrix, ρ, as

$$\tilde{\rho} = 3\hat{\rho}^2 - 2\hat{\rho}^3 \tag{9}$$

The modified grand potential is then defined as

$$\tilde{\Omega} = tr[\tilde{\rho}(\hat{H}-\mu)] \tag{10}$$

$$= tr[(3\hat{\rho}^2-2\hat{\rho}^3)(\hat{H}-\hat{\mu})] \tag{11}$$

$$= tr[(3\hat{\rho}^2-2\hat{\rho}^3)\hat{H}'] \tag{12}$$

where

$$\hat{H}' = \hat{H} - \mu \tag{13}$$

(Gradient)

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

$$= tr[3(\hat{H}'\hat{\rho}+\hat{\rho}\hat{H}')\delta\hat{\rho} - 2(\hat{H}'\hat{\rho}^2+\hat{\rho}\hat{H}'\hat{\rho}+\hat{\rho}^2\hat{H}')\delta\hat{\rho}] \tag{14}$$

(☺ cyclic shifts)

Note that the gradient is defined as

$$\delta\tilde{\Omega} = tr\left(\frac{\partial\tilde{\Omega}}{\partial\hat{\rho}}\delta\hat{\rho}\right) = \sum_{ij}\left(\frac{\partial\tilde{\Omega}}{\partial\rho}\right)_{ij}\delta\rho_{ji} \tag{15}$$

Comparing Eqs. (14) and (15),

$$\frac{\partial\tilde{\Omega}}{\partial\hat{\rho}} = 3(\hat{H}'\hat{\rho}+\hat{\rho}\hat{H}') - 2(\hat{H}'\hat{\rho}^2+\hat{\rho}\hat{H}'\hat{\rho}+\hat{\rho}^2\hat{H}') \tag{16}$$

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

(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,

$$\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}} = 6\hat{\rho}\hat{H}' - 6\underbrace{\hat{\rho}^2}_{=\hat{\rho}}\hat{H}' = 0 \quad //$$

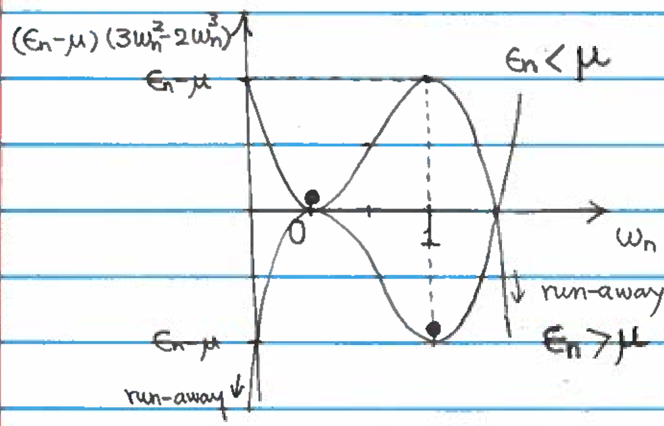
(minimum)

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

$$\hat{\rho} = \sum_n |n\rangle w_n \langle n| \tag{17}$$

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

$$\tilde{\Omega} = \sum_n (\epsilon_n - \mu)(3w_n^2 - 2w_n^3) \tag{18}$$



The minimum of this function is w

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

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

$$\Omega_{gs} = \sum_n (\epsilon_n - \mu)\Theta(\mu - \epsilon_n) \tag{19}$$

(single minimum)

Since $\tilde{\Omega}$ 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, ρ_{ij} can be approximated as

$$\rho_{ij} = 0 \qquad (\forall R_{ij} > R_c) \tag{20}$$

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

$$\tilde{\Omega} = tr[(3\hat{\rho}^2 - 2\hat{\rho}^3)(\hat{H} - \mu)] \tag{21}$$

with respect to ρ_{ij} with constraint

$$\rho_{ij} = 0 \quad (\forall R_{ij} > R_c) \tag{22}$$

using the conjugate gradient algorithm with gradient

$$\frac{\partial \tilde{\Omega}}{\partial \hat{\rho}} = 3(\hat{H}'\hat{\rho} + \hat{\rho}\hat{H}') - 2(\hat{H}'\hat{\rho}^2 + \hat{\rho}\hat{H}'\hat{\rho} + \hat{\rho}^2\hat{H}') \tag{23}$$

— On the constrained minimization, Eq.(7)

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

$$\Omega = \mathrm{tr}[\hat{\rho}(\hat{H}-\mu)] \tag{24}$$

with idempotency constraint

$$\hat{\rho}^2 - \hat{\rho} = 0 \tag{25}$$

To solve this problem, we introduce Lagrange multipliers

$$\Omega' = \mathrm{tr}[\hat{\rho}(\hat{H}-\mu) - \hat{\Lambda}(\hat{\rho}^2 - \hat{\rho})] \tag{26}$$

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

$$\frac{\partial\Omega'}{\partial\hat{\Lambda}} = \hat{\rho}^2 - \hat{\rho} = 0 \tag{27}$$

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

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

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

$$\therefore \frac{\partial\Omega'}{\partial\hat{\rho}} = \hat{H} - \mu - (\hat{\Lambda}\hat{\rho} + \hat{\rho}\hat{\Lambda} - \hat{\Lambda}) = 0 \tag{28}$$

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

$\langle n| \times$ Eq.(27) $\times |n\rangle$

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

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

$\langle n| \times$ Eq.(27) $\times |n\rangle$

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

$$\therefore \Lambda_{nn} = \begin{cases} H_{nn} - \mu & (\rho_n = 1) \\ \mu - H_{nn} & (\rho_n = 0) \end{cases}$$

McWeeny "purification" fixed-point iteration