Local-Orbital-Minimization O(N) DFT

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- Summary of nonorthogonal-orbital DFT

(Problem) Minimize unconstrainedly,

$$\begin{cases} E[\{\phi_i(\mathbf{r})\}] = \sum_i \sum_j S^{-1}_{ij} \langle \phi_j | \frac{\hat{p}^2}{2m} | \phi_i \rangle + F[\rho(\mathbf{r})] & (1) \\ F[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + F_{xc}[\rho(\mathbf{r})] & (2) \\ \rho(\mathbf{r}) = \sum_{ij} S^{-1}_{ij} \phi^*_j(\mathbf{r}) \phi_i(\mathbf{r}) & (3) \end{cases}$$

The above relations can be derived from the single-particle density matrix operator (or projection to the occupied states),

$$\boxed{\hat{\rho} = \sum_{i,j} |\phi_i\rangle S^{-1}_{ij} \langle \phi_j |} \quad (4)$$

∵

$$\rho(\mathbf{r}) = \langle r | \hat{\rho} | \mathbf{r} \rangle = \sum_{i,j} \underbrace{\langle \mathbf{r} | \phi_i \rangle}_{\phi_i(\mathbf{r})} S^{-1}_{ij} \underbrace{\langle \phi_j | \mathbf{r} \rangle}_{\phi^*_j(\mathbf{r})} = \sum_{ij} S^{-1}_{ij} \phi^*_j(\mathbf{r}) \phi_i(\mathbf{r})$$

$$E_{kin} = \mathrm{Tr} \frac{\hat{p}^2}{2m} \hat{\rho}$$

$$= \int d\mathbf{r} \sum_{i,j} \langle \mathbf{r} | \frac{\hat{p}^2}{2m} | \phi_i \rangle S^{-1}_{ij} \langle \phi_j | \mathbf{r} \rangle$$

$$= \sum_{ij} S^{-1}_{ij} \underbrace{\int d\mathbf{r} \langle \phi_j | \mathbf{r} \rangle \langle \mathbf{r} |}_{1} \frac{\hat{p}^2}{2m} | \phi_i \rangle$$

$$= \sum_{ij} S^{-1}_{ij} \langle \phi_j | \frac{\hat{p}^2}{2m} | \phi_i \rangle \quad //$$

※ O(N) strategy derives from the short range of $\hat{\rho}$ for localized $|\phi_i\rangle$'s. In principle S^{-1}_{ij} involves $O(N^3)$ computation, but we should be able to truncate it to O(N).

— Mauri-Galli-Car Energy Functional

[F. Mauri, G. Galli, and R. Car, PRB 47, 9973 ('93)]

This energy functional can be formally derived by expanding $\mathbb{S}^{-1}$ in $\mathbb{I}-\mathbb{S}$:

$$\mathbb{S}^{-1} = \left[\mathbb{I} - (\mathbb{I}-\mathbb{S})\right]^{-1} = \sum_{n=0}^{\infty} (\mathbb{I}-\mathbb{S})^n \tag{5}$$

$$\cong \mathbb{I} + (\mathbb{I}-\mathbb{S}) + O\left((\mathbb{I}-\mathbb{S})^2\right)$$

$$= 2\mathbb{I} - \mathbb{S} \tag{6}$$

Substituting Eq. (6) in Eqs. (1) − (3),

$$E[\{\phi_i(\mathbf{r})\}] = \sum_{i,j} (2\delta_{ij} - S_{ij}) \langle\phi_j|\frac{\hat{p}^2}{2m}|\phi_i\rangle + F[\rho(\mathbf{r})] \tag{7}$$

$$F[\rho(\mathbf{r})] = \int d\mathbf{r}\,\rho(\mathbf{r})\,v_{ext}(\mathbf{r}) + \frac{e^2}{2}\int d\mathbf{r}\,d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + F_{xc}[\rho(\mathbf{r})] \tag{8}$$

$$\rho(\mathbf{r}) = \sum_{ij} (2\delta_{ij} - S_{ij})\,\phi_j^*(\mathbf{r})\,\phi_i(\mathbf{r}) \tag{9}$$

$$S_{ij} = \langle\phi_i|\phi_j\rangle \tag{10}$$

– Kim-Mauri-Galli energy functional

[J. Kim, F. Mauri, and G. Galli, PRB 52, 1640 (192)]

Instead of the total energy, we can minimize the "band-structure" energy,

$$E_{BS}[\{\psi_i(\mathbf{r})\}] = \sum_i \langle\psi_i|\frac{\hat{p}^2}{2m}|\psi_i\rangle + \int d\mathbf{r}\, \psi_i^*(\mathbf{r})\frac{\delta F}{\delta\psi_i^*(\mathbf{r})} \tag{11}$$

where $\psi_i(\mathbf{r})$ are orthogonal orbitals.

$$\frac{\delta F}{\delta\psi_i^*(\mathbf{r})} = \int d\mathbf{r}' \underbrace{\frac{\delta\rho(\mathbf{r}')}{\delta\psi_i^*(\mathbf{r})}}_{\delta(\mathbf{r}-\mathbf{r}')\psi_i(\mathbf{r}')} \frac{\delta F}{\delta\rho(\mathbf{r}')} = \frac{\delta F}{\delta\rho(\mathbf{r})}\psi_i(\mathbf{r})$$

$$= \Bigg[\underbrace{v_{ext}(\mathbf{r}) + e^2\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta F_{xc}}{\delta\rho(\mathbf{r})}}_{v(\mathbf{r})}\Bigg]\psi_i(\mathbf{r})$$

$$\therefore \begin{cases} E_{BS}[\{\psi_i(\mathbf{r})\}] = \sum_i \langle\psi_i|\hat{H}|\psi_j\rangle & (12) \\ \hat{H} = \dfrac{\hat{p}^2}{2m} + v(\mathbf{r}) & (13) \\ v(\mathbf{r}) \doteq v_{ext}(\mathbf{r}) + e^2\displaystyle\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta F_{xc}}{\delta\rho(\mathbf{r})} & (14) \end{cases}$$

Using nonorthogonal orbitals,

$$|\psi_i\rangle = \sum_j |\phi_j\rangle S_{ji}^{-1/2} \tag{15}$$

and

$$\langle\psi_i| = \sum_j (S_{ji}^{-1/2})^* \langle\phi_j| = \sum_j S_{ij}^{-1/2}\langle\phi_j|, \tag{16}$$

the band-structure energy is rewritten as

$$E_{BS} = \sum_i \sum_j S^{-1/2}_{ij} \langle \phi_j | \hat{H} \left(\sum_k | \phi_k \rangle S^{-1/2}_{ki} \right)$$

$$= \sum_{jk} \underbrace{\left(\sum_i S^{-1/2}_{ki} S^{-1/2}_{ij} \right)}_{S^{-1}_{kj}} \langle \phi_j | \hat{H} | \phi_k \rangle \qquad (17)$$

(Nonorthogonal band-structure energy functional)

$$E_{BS}[\{\phi_i^*(\mathbf{r})\}] = \sum_{ij} S^{-1}_{ij} \langle \phi_j | \hat{H} | \phi_i \rangle \qquad (18)$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + v(\mathbf{r}) \qquad (19)$$

$$v(\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta F_{xc}}{\delta \rho(\mathbf{r})} \qquad (20)$$

$$\rho(\mathbf{r}) = \sum_{ij} S^{-1}_{ij} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) \qquad (21)$$

The Kim-Mauri-Galli energy functional is formally derived by replacing $\mathbb{S}^{-1} \longrightarrow 2\mathbb{I} - \mathbb{S}$.

$$E_{BS}[\{\phi_i^*(\mathbf{r})\}] = \sum_{ij} (2\delta_{ij} - S_{ij}) \langle \phi_i | \hat{H} | \phi_j \rangle \tag{22}$$

$$\hat{H} = \frac{\hat{P}^2}{2m} + v(\mathbf{r}) \tag{23}$$

$$v(\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta F_{xc}}{\delta \rho(\mathbf{r})} \tag{24}$$

$$\rho(\mathbf{r}) = \sum_{ij} (2\delta_{ij} - S_{ij}) \, \phi_j^*(\mathbf{r}) \, \phi_i(\mathbf{r}) \tag{25}$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{26}$$

— Properties of the Kim-Mauri-Galli energy functional

(i) $E_{BS}[\{\phi_i(\mathbf{r})\}]$ is invariant under unitary operations of type

$$\begin{cases} |\phi_i'\rangle = \sum_{j=1}^{N} U_{ij} |\phi_j\rangle & (27) \\ U_{ij}^{-1} = U_{ji}^{*} \quad \left(\langle u_j | u_k \rangle = \sum_i \overbrace{U_{ij}^{*}}^{U_{ji}^{-1}} U_{ik} = \delta_{jk} \sim \text{orthonormal} \right) & (28) \end{cases}$$

∵

$$\hat{\rho}' = \sum_{ij} |\phi_i'\rangle (2\delta_{ij} - \langle \phi_i' | \phi_j' \rangle) \langle \phi_j' |$$

$$= \sum_{ij} \sum_k U_{ik} |\phi_k\rangle \left[2\delta_{ij} - \sum_l \langle \phi_l | \overbrace{U_{il}^{*}}^{U_{li}^{-1}} \left(\sum_m U_{jm} |\phi_m\rangle \right) \right] \sum_n \langle \phi_n | \overbrace{U_{jn}^{*}}^{U_{nj}^{-1}}$$

$$= \sum_{kn} |\phi_k\rangle \left[\sum_{ij} U_{ik} 2\delta_{ij} U_{nj}^{-1} - \sum_{ij} \sum_{lm} U_{ik} U_{li}^{-1} \langle \phi_l | \phi_m \rangle U_{jm} U_{nj}^{-1} \right] \langle \phi_n |$$

$$= \sum_{kn} |\phi_k\rangle \Big[2 \underbrace{\sum_i U_{ni}^{-1} U_{ik}}_{\delta_{kn}} - \underbrace{\sum_{lm} \underbrace{\Big(\sum_i U_{li}^{-1} U_{ik}\Big)}_{\delta_{lk}} \underbrace{\Big(\sum_j U_{nj}^{-1} U_{jm}\Big)}_{\delta_{nm}} \langle \phi_l | \phi_m \rangle}_{\langle \phi_k | \phi_n \rangle} \Big] \langle \phi_n |$$

$$= \sum_{kn} |\phi_k\rangle (2\delta_{kn} - S_{kn}) \langle \phi_n | = \hat{\rho} \qquad //$$

(ii) The ground-state energy $E_{BS}^{\emptyset}$ is a stationally point of $E_{BS}[\{\phi_i(\mathbf{r})\}]$.

∵ The gradient of the functional is,

$$\boxed{\begin{aligned} \frac{\delta E_{BS}}{\delta\langle\phi_i|} &= \sum_j (2\delta_{ij} - S_{ij})\hat{H}|\phi_j\rangle - \sum_j |\phi_j\rangle\langle\phi_i|\hat{H}|\phi_j\rangle && (27) \\ &= 2\hat{H}|\phi_i\rangle - \sum_j S_{ij}\hat{H}|\phi_j\rangle - \sum_j \langle\phi_i|\hat{H}|\phi_j\rangle|\phi_j\rangle && (28) \end{aligned}}$$

When $|\phi_i\rangle = |\chi_i\rangle$, orthonormal eigen functions of $\hat{H}$, i.e,

$$\hat{H}|\chi_i\rangle = \epsilon_i|\chi_i\rangle, \tag{29}$$

and $\langle\chi_i|\chi_j\rangle = \delta_{ij}$, then

$$\frac{\delta E_{BS}}{\delta\langle\chi_i|} = \cancel{2\epsilon_i|\chi_i\rangle} - \underbrace{\sum_j \delta_{ij}\epsilon_j|\chi_j\rangle}_{\cancel{\epsilon_i|\chi_i\rangle}} - \underbrace{\sum_j \epsilon_j \underbrace{\langle\chi_i|\chi_j\rangle}_{\delta_{ij}}|\chi_j\rangle}_{\cancel{\epsilon_i|\chi_i\rangle}} = 0$$

The stationally value is

$$E_{BS} = \sum_{ij}\underbrace{(2\delta_{ij} - \underbrace{\langle\chi_i|\chi_j\rangle}_{\delta_{ij}})}_{\delta_{ij}}\underbrace{\langle\chi_i|\hat{H}|\chi_j\rangle}_{\epsilon_j\underbrace{\langle\chi_i|\chi_j\rangle}_{\delta_{ij}}} = \sum_{ij}\epsilon_j\delta_{ij} = \sum_i \epsilon_i,$$

i.e, the ground-state band-structure energy. //

(iii) The ground-state energy, $E_{BS}^{\emptyset}$, is a minimum of $E_{BS}[\{\phi_i(\mathbf{r})\}]$.
We consider that one of the occupied state is mixed with an unoccupied state.

$$|\chi_J\rangle \rightarrow \cos(x)\,|\chi_J\rangle + \sin(x)\,|\chi_I\rangle \tag{30}$$

$$\begin{cases} \langle\chi_J|\chi_J\rangle = \cos^2(x) + \sin^2(x) = 1 \\ \langle\chi_i|\chi_J\rangle = \emptyset \end{cases} \longrightarrow \langle\chi_i|\chi_j\rangle = \delta_{ij} \text{ is conserved.}$$

$$\begin{aligned} \therefore\ \delta E_{BS} &= \delta\langle\chi_J|\hat{H}|\chi_J\rangle \\ &= \cos^2(x)\,\epsilon_J + \sin^2(x)\,\epsilon_I - \epsilon_J \\ &= \left[\left(1 - \frac{x^2}{2} + \cdots\right)^2 - 1\right]\epsilon_J + (x + \cdots)^2\,\epsilon_I \\ &= x^2(\epsilon_I - \epsilon_J) > 0 \end{aligned}$$

i.e., $E_{BS}[\{\phi_i(\mathbf{r})\}]$ is positive definite for a small mixture of unoccupied states. //

Local-Orbital-Based O(N) Density Functional Theory: Ordejón-Drabold-Martin-Grumbach Formulation

1/2/00

– Orthogonal DFT: constrained minimization

(Problem) Minimize the band-structure energy,

$$E_{BS}[\{\psi_i(\mathbf{r})\}] = \sum_{i=1}^{N} \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right] \psi_i(\mathbf{r}), \tag{1}$$

where

$$\begin{cases} v(\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \dfrac{\delta F_{xc}}{\delta \rho(\mathbf{r})}, & (2) \\ \rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}), & (3) \end{cases}$$

with orthonormal constraints,

$$S_{ij} = \langle \psi_i | \psi_j \rangle = \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij} \tag{4}$$

– Lagrange-multiplier method

The above constrained minimization is equivalent to the following unconstrained minimization with extra N^2 independent variables, Λ_{ij}, the Lagrange multipliers.

$$\tilde{E}[\{\psi_i(\mathbf{r})\}] = \sum_{i=1}^{N} \langle \psi_i | \hat{H} | \psi_i \rangle - \sum_{i,j=1}^{N} \Lambda_{ji} (S_{ij} - \delta_{ij}) \tag{5}$$

The solution is obtained by requiring $\tilde{E}$ to be stationary in both $|\psi_i\rangle$ and Λ_{ji}:

$$\begin{cases} \dfrac{\delta \tilde{E}}{\delta \langle \psi_i |} = \hat{H} |\psi_i\rangle - \sum_{j=1}^{N} \Lambda_{ji} |\psi_j\rangle = 0 & (6) \\ \dfrac{\delta \tilde{E}}{\partial \Lambda_{ij}} = S_{ij} - \delta_{ij} = 0 & (7) \end{cases}$$

Equation (6) can be cast into a matrix equation,

$\langle \psi_k | \times$ Eq. (6)

$$\langle \psi_k | \hat{H} | \psi_i \rangle - \sum_j \Lambda_{ji} \langle \psi_k | \psi_j \rangle = 0$$

$$H_{ki} - \sum_j \Lambda_{ji} S_{kj} = 0 \tag{8}$$

or

$$\mathbb{H} - \mathbb{S}\mathbb{\Lambda} = 0 \tag{9}$$

This equation define the relation between $|\psi_i\rangle$ and Λ_{ij} for the solution of the problem. For the solution, Eq. (7) must be satisfied so that $\mathbb{S} = \mathbb{I}$. Substituting this in Eq. (9),

$$\mathbb{H} = \mathbb{\Lambda} \quad \text{or} \quad \langle \psi_i | \hat{H} | \psi_j \rangle = \Lambda_{ij} \tag{10}$$

– Ordejón – Drabold – Martin – Grumbach energy functional
[P. Ordejón, D.A. Drabold, R.M. Martin, & M.P. Grumbach, PRB 51, 1456 ('95)]

For arbitrary nonorthogonal orbitals, $|\phi_i\rangle$, we use the Lagrange multiplier of Eq. (10), though which is only valid for the double-stationary solution of Eq. (5).

$$E[\{|\phi_i\rangle\}] = \sum_{i=1}^{N} \langle\phi_i|\hat{H}|\phi_i\rangle - \sum_{i,j=1}^{N} \langle\phi_j|\hat{H}|\phi_i\rangle (S_{ij} - \delta_{ij}) \tag{11}$$

$$= \sum_{i,j=1}^{N} (2\delta_{ij} - S_{ij}) \langle\phi_j|\hat{H}|\phi_i\rangle \tag{12}$$

※ This functional is equivalent to the Mauri–Galli–Car functional derived from the Taylor expansion of $\mathbb{S}^{-1}$.

$$|G_i\rangle \equiv -\frac{\delta E}{\delta\langle\phi_i|}$$

$$= \underbrace{-\hat{H}|\phi_i\rangle}_{\text{physical force}} + \underbrace{\sum_{j=1}^{N} \hat{H}|\phi_j\rangle(S_{ji} - \delta_{ji}) + \sum_{j=1}^{N} H_{ji}|\phi_j\rangle}_{\text{constraint force}} \tag{13}$$

Explicit orthonormalization is not required since the constraint force will purify the orbitals.

Properties of Ordejón–Drabold–Martin–Grumbach Functional

1/3/00

— Problem

Perform unconstrained minimization of the energy functional

$$\begin{cases} E[\{|\phi_i\rangle\}] = \sum_{i=1}^{N} \langle\phi_i|\hat{H}|\phi_i\rangle - \sum_{i,j=1}^{N} \langle\phi_j|\hat{H}|\phi_i\rangle (S_{ij} - \delta_{ij}) & (1) \\ S_{ij} = \langle\phi_i|\phi_j\rangle & (2) \end{cases}$$

The gradient of the second term is the constraint force, which, at the stationary solution, automatically enforces the orthonormality.

— Properties

(i) The functional is invariant under unitary transformations,

$$\begin{cases} |\phi_i'\rangle = \sum_{j=1}^{N} U_{ij} |\phi_j\rangle \quad (i = 1, \ldots, N) & (3) \\ \sum_{i=1}^{N} \underbrace{U_{ij}^*}_{U_{ji}^{-1}} U_{ik} = \langle u^{(j)} | u^{(k)} \rangle = \delta_{jk} \leftrightarrow U_{ij}^{-1} = U_{ji}^* & (4) \end{cases}$$

☺ See 1/1/00. //

(ii) E is stationary at the correct ground state of $\hat{H}$.

☺ See 1/1/00. //

In order to prove further properties, assume that the Hamiltonian is defined in an M-dimensional space, where $M\ (\geq N)$ is the size of the basis set (either M grid points or M atomic orbitals for LCAO).

Let's expand the N nonorthogonal orbitals, $|\phi_i\rangle$, in terms of the eigenvectors of $\hat{H}$:

$$|\phi_i\rangle = \sum_{j=1}^{M} a_{ij} \, |\psi_j\rangle \quad (i = 1, \ldots, N) \tag{5}$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{6}$$

$$\hat{H} |\psi_i\rangle = \epsilon_i \, |\psi_i\rangle \tag{7}$$

where $\{\epsilon_i \,|\, i = 1, \ldots, N\}$ are occupied $\{\epsilon_i \,|\, i = N+1, \ldots, M\}$ are unoccupied eigenenergies.

Substituting Eq. (5) in (1) (assume a_{ij} are real),

$$E = \sum_{i=1}^{N} \sum_{k=1}^{M} \sum_{l=1}^{M} a_{ik} a_{il} \underbrace{\langle \psi_k | \hat{H} | \psi_l \rangle}_{\epsilon_k \delta_{kl}}$$

$$- \sum_{i,j=1}^{N} \sum_{k,l=1}^{M} a_{jk} a_{il} \underbrace{\langle \psi_k | \hat{H} \psi_l \rangle}_{\epsilon_k \delta_{kl}} \left(\sum_{m,n=1}^{M} a_{im} a_{jn} \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} - \delta_{ij} \right)$$

$$= \sum_{i=1}^{N} \sum_{k=1}^{M} a_{ik}^2 \epsilon_k - \sum_{i,j=1}^{N} \sum_{k=1}^{M} a_{jk} a_{ik} \epsilon_k \left(\sum_{m=1}^{M} a_{im} a_{jm} - \delta_{ij} \right)$$

$$E = \sum_{i=1}^{N}\sum_{k=1}^{M} a_{ik}^2 \epsilon_k - \sum_{i,j=1}^{N}\sum_{k,m=1}^{M} \epsilon_k a_{jk} a_{ik} a_{im} a_{jm} + \sum_{i=1}^{N}\sum_{k=1}^{M} a_{ik}^2 \epsilon_k$$

$$= 2\sum_{k=1}^{M}\epsilon_k \sum_{i=1}^{N} a_{ik}^2 - \sum_{k=1}^{M}\epsilon_k \sum_{m=1}^{M} \underbrace{\left(\sum_{i=1}^{N} a_{ik}a_{im}\right)\left(\sum_{j=1}^{N} a_{jk}a_{jm}\right)}_{\left(\sum_{i=1}^{N} a_{ik}a_{im}\right)^2}$$

$$= 2\sum_{k=1}^{M}\epsilon_k \sum_{i=1}^{N} a_{ik}^2 - \sum_{k=1}^{M}\epsilon_k \sum_{m=1}^{M} \left\{ \left[\sum_{i=1}^{N} a_{ik}a_{im} - \delta_{km}\right]^2 + 2\delta_{km}\sum_{i=1}^{N} a_{ik}a_{im} - \delta_{km} \right\}$$

$$= \cancel{2\sum_{k=1}^{M}\epsilon_k \sum_{i=1}^{N} a_{ik}^2} - \sum_{k=1}^{M}\epsilon_k \sum_{m=1}^{M}\left[\sum_{i=1}^{N} a_{ik}a_{im} - \delta_{km}\right]^2 - \cancel{2\sum_{k=1}^{M}\epsilon_k \sum_{i=1}^{N} a_{ik}^2} + \sum_{k=1}^{M}\epsilon_k$$

$$\therefore \quad \boxed{E[\{a_{ik}\}] = \sum_{k=1}^{M}\epsilon_k - \sum_{k=1}^{M}\epsilon_k \sum_{m=1}^{M}\Big[\underbrace{\sum_{i=1}^{N} a_{ik}a_{im}}_{({}^{T}AA)_{km}} - \delta_{km}\Big]^2} \qquad (8)$$

If $|\phi_i\rangle$ are N-lowest lying orthonormal states, $|\psi_i\rangle$ $(i=1,\dots,N)$, then

$$a_{ik} = \begin{cases} \delta_{ik} & (k=1,\dots,N) \\ 0 & (k=N+1,\dots,M) \end{cases} \qquad \begin{array}{c|cc} & 1 \;\cdots\; N & N+1 \;\cdots\; M \\ \hline 1 & 1 & \\ & \ddots & \emptyset \\ N & 1 & \end{array} \qquad (9)$$

Substituting Eq. (9) in (8)

$$\underset{N}{\left[\begin{array}{c|c} 1 \ddots 1 & \emptyset \end{array}\right]}^{M} \left[\begin{array}{c} 1 \ddots 1 \\ \hline \emptyset \end{array}\right]^{N}_{M} = \left[\begin{array}{c|c} 1 \ddots 1 & \emptyset \\ \hline \emptyset & \emptyset \end{array}\right]^{M}_{M}$$

$$E = \sum_{k=1}^{M}\epsilon_k - \sum_{k=1}^{M}\epsilon_k \sum_{m=1}^{M}\Big[\underbrace{\sum_{i=1}^{N} a_{ik}a_{im}}_{} - \delta_{km}\Big]^2$$

$$\underbrace{({}^{T}AA)_{km} = \begin{matrix} \delta_{km} & \text{if } k,m \le N \\ 0 & \text{else} \end{matrix}}$$

$$\delta_{k,m} \quad \text{not if } k,m \le N \to \begin{array}{c|cc} & 1 \;\; N & N+1 \;\; M \\ \hline 1 \;\; N & \emptyset & \emptyset \\ N+1 & & 1 \\ & \emptyset & \ddots \\ M & & 1 \end{array}$$

$$= \sum_{k=1}^{M}\epsilon_k - \underbrace{\sum_{k,m=N+1}^{M}\epsilon_k \delta_{k,m}}_{\sum_{k=N+1}^{M}\epsilon_k}$$

$$= \sum_{k=1}^{N}\epsilon_k$$

i.e. the functional gives the correct ground-state energy.

(iii) The energy functional has a lower bound if and only if all the N eigenvalues of $\hat{H}$ are negative (unlikely).

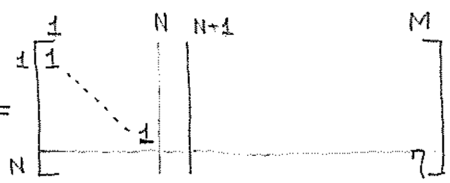
$\longrightarrow$ Motivate shifted version, $\hat{H}' = \hat{H} - \mu \hat{I}$

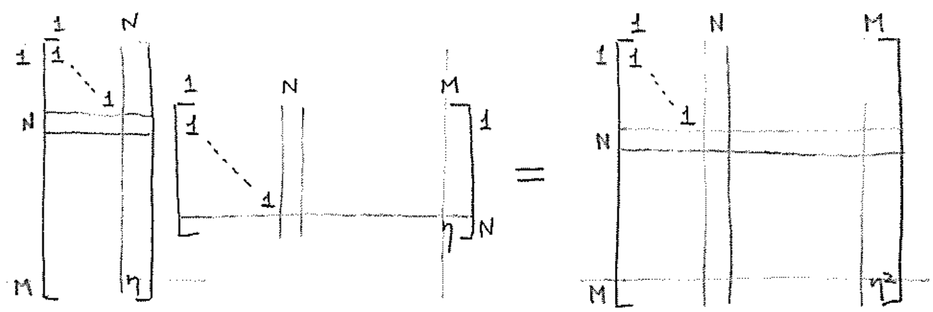
☹

Let's assume all but one (the M-th) eigenvalues are negative and choose

$$\begin{cases} |\varphi_i\rangle = |\psi_i\rangle & (i = 1, \dots, N-1) \\ |\varphi_N\rangle = \eta\, |\psi_M\rangle \end{cases} \tag{10}$$

or

$A =$ 

$^TAA =$ 

i.e. $\sum_{i=1}^{N} {}^Ta_{ki}\, a_{im}$ project only $\{|\psi_i\rangle \mid i = 1, \dots, N-1\}$ fully and $|\psi_M\rangle$ partially.

$$\therefore E = \sum_{k=1}^{M} \epsilon_k - \sum_{k=1}^{M} \epsilon_k \sum_{m=1}^{M} \underbrace{\left[({}^TAA)_{km} - \delta_{km} \right]^2}_{\delta_{km}\theta(N \le k, m \le M-1) \; + \; (\eta^2 - 1)^2 \delta_{kM} \delta_{mM}}$$

$$= \sum_{k=1}^{M} \epsilon_k - \sum_{k=N}^{M-1} \epsilon_k - \epsilon_M (\eta^2 - 1)^2$$

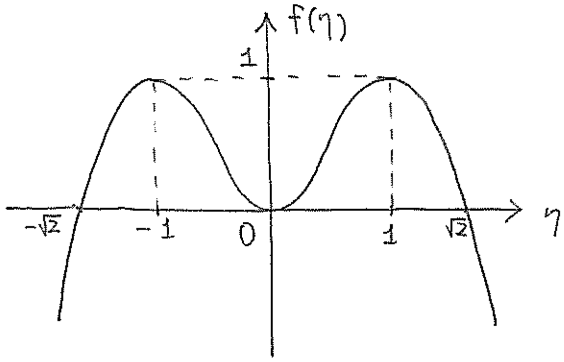
$$= \sum_{k=1}^{N-1} \epsilon_k + \epsilon_M \left[1 - (\eta^2 - 1)^2 \right]$$

$$= \sum_{k=1}^{N-1} \epsilon_k + \epsilon_M (-\eta^4 + 2\eta^2) \tag{11}$$

Consider

$$\begin{cases} f(\eta) = -\eta^4 + 2\eta^2 & (12) \\ f'(\eta) = -4\eta^3 + 4\eta = -4\eta(\eta-1)(\eta+1) & (13) \end{cases}$$

η	$\cdots$	-1	$\cdots$	$\emptyset$	$\cdots$	1	$\cdots$
f'	$+$	0	$-$	0	$+$	0	$-$
f	$\nearrow$	1	$\searrow$	$\emptyset$	$\nearrow$	1	$\searrow$



The energy function $E(\eta)$ has a local minimum at $\eta = 0$, but also has a <u>run-away solution</u>!

$$E(\eta) = \sum_{k=1}^{N-1} \epsilon_k + \epsilon_M(-\eta^4 + 2\eta^2) \longrightarrow -\infty \quad (\eta \to \pm\infty) \tag{14}$$

— (Lesson)

Initial N orbitals must not be random, but reasonably close to the eigenstates (localized rather than plane wave).

iv) Even if some of the empty eigenvalues of $\hat{H}$ are negative, the functional has a <u>local minimum</u> for the ground state, provided that all the occupied states are negative.
(OK for condensed-matter ground states.)

Let's perturb the ground state

$$a_{ik} = \begin{cases} \delta_{ik} + \epsilon_{ik} & k = 1, \dots, N \\ \epsilon_{ik} & k = N+1, \dots, M \end{cases} \tag{15}$$

or

$$\mathbb{A} = \mathbb{I}_N + \mathcal{E} \tag{16}$$

$$^T\!\mathbb{A}\,\mathbb{A} = \mathbb{I}_N + (\mathbb{I}_N \mathcal{E} + {}^T\!\mathcal{E}\, \mathbb{I}_N) + {}^T\!\mathcal{E}\,\mathcal{E} \tag{17}$$

Here,

$$\mathbb{I}_N \mathcal{E} = \begin{array}{cc} & \begin{array}{cc} 1 & N \end{array} \\ \begin{array}{c} 1 \\ N \\ \\ M \end{array} & \left[\begin{array}{c} \begin{matrix} 1 & & \\ & \ddots & \\ & & 1 \end{matrix} \\ \hline \varnothing \end{array}\right] \end{array} \begin{array}{cc} & \begin{array}{ccc} 1 & N & M \end{array} \\ \begin{array}{c} 1 \\ N \end{array} & \left[\begin{array}{c|c} \quad & \mathcal{E} \end{array}\right] \end{array} = \begin{array}{cc} & \begin{array}{ccc} 1 & N & M \end{array} \\ \begin{array}{c} 1 \\ N \\ M \end{array} & \left[\begin{array}{c|c} \mathcal{E} & \mathcal{E} \\ \hline \varnothing & \varnothing \end{array}\right] \end{array}$$

$$\therefore\ \mathbb{I}_N \mathcal{E} + \mathcal{E}\, \mathbb{I}_N = \begin{array}{cc} & \begin{array}{ccc} 1 & N & M \end{array} \\ \begin{array}{c} 1 \\ N \\ M \end{array} & \left[\begin{array}{c|c} {}^T\!\mathcal{E} + \mathcal{E} & \mathcal{E} \\ \hline {}^T\!\mathcal{E} & \varnothing \end{array}\right] \end{array}$$

$$\therefore\ {}^T\!\mathbb{A}\,\mathbb{A} - \mathbb{I}_M = \begin{array}{cc} & \begin{array}{ccc} 1 & N & M \end{array} \\ \begin{array}{c} 1 \\ N \\ M \end{array} & \left[\begin{array}{c|c} \varnothing & \varnothing \\ \hline \varnothing & -\mathbb{I} \end{array}\right] \end{array} + \left[\begin{array}{c|c} {}^T\!\mathcal{E} + \mathcal{E} & \mathcal{E} \\ \hline {}^T\!\mathcal{E} & \varnothing \end{array}\right] + \left[\ {}^T\!\mathcal{E}\,\mathcal{E}\ \right]$$

$$\therefore\; E = \sum_{k=1}^{M} \epsilon_k - \sum_{k=1}^{M} \epsilon_k \sum_{m=1}^{M} \left[\left({}^{T}\!\mathbb{A}\mathbb{A} - \mathbb{I}_M \right)_{km} \right]^2$$

$$= \sum_{k=1}^{M} \epsilon_k - \sum_{k,m=1}^{N} \epsilon_k \left(\epsilon_{km} + \epsilon_{mk} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2$$

$$- \sum_{k=1}^{N} \sum_{m=N+1}^{M} \epsilon_k \left(\epsilon_{km} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2$$

$$- \underbrace{\sum_{k=N+1}^{M} \sum_{m=1}^{N} \epsilon_k \left(\epsilon_{mk} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2}_{k \leftrightarrow m \quad \sum_{k=1}^{N} \sum_{m=N+1}^{M} \epsilon_m \left(\epsilon_{km} + \sum_{i=1}^{N} \epsilon_{im}\epsilon_{ik} \right)^2}$$

$$- \sum_{k,m=N+1}^{M} \epsilon_k \underbrace{\left(-\delta_{km} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2}_{\delta_{km} - 2\delta_{km}\left(\sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im}\right) + \left(\sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im}\right)^2}$$

$$= \sum_{k=1}^{N} \epsilon_k - \sum_{k,m=1}^{N} \overset{\text{occ}}{\epsilon_k} \left(\epsilon_{km} + \epsilon_{mk} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2$$

$$- \sum_{k=1}^{N} \sum_{m=N+1}^{M} \left(\overset{\text{occ}}{\epsilon_k} + \overset{\text{unocc}}{\epsilon_m} \right) \left(\epsilon_{km} + \sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2$$

$$+ \sum_{k=N+1}^{M} 2\overset{\text{unocc}}{\epsilon_k} \left(\sum_{i=1}^{N} \epsilon_{ik}^2 \right) - \sum_{k,m=N+1}^{M} \epsilon_k \left(\sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im} \right)^2 \qquad (18)$$

In the second-order of $\mathcal{E}$ (there is no first-order $\leftrightarrow$ stationary),

$$E-\sum_{k=1}^{N}\epsilon_k = -\sum_{k,m=1}^{N}\overset{\text{occ}}{\epsilon_k}\left(\epsilon_{km}+\epsilon_{mk}\right)^2$$

$$-\sum_{k=1}^{N}\sum_{m=N+1}^{M}\left(\overset{\text{occ}}{\epsilon_k}+\overset{\text{unocc}}{\epsilon_m}\right)\epsilon_{km}^2$$

$$+\underbrace{\sum_{i=1}^{N}\sum_{k=N+1}^{M}2\overset{\text{unocc}}{\epsilon_k}\,\epsilon_{ik}^2}_{\sum_{k=1}^{N}\sum_{m=N+1}^{M}2\epsilon_m\epsilon_{km}^2}$$

$$\therefore E-\sum_{k=1}^{N}\epsilon_k = -\sum_{k,m=1}^{N}\underbrace{\overset{\text{occ}}{\epsilon_k}}_{\substack{\text{negative if all occupied}\\ \text{states are negative.}}}\left(\epsilon_{km}+\epsilon_{mk}\right)^2-\sum_{k=1}^{N}\sum_{m=N+1}^{M}\underbrace{\left(\overset{\text{occ}}{\epsilon_k}-\overset{\text{unocc}}{\epsilon_m}\right)}_{\text{negative-definite}}\epsilon_{km}^2 \qquad (19)$$

This is guaranteed to be positive definite only if all the "occupied" states are negative.

If

$$\mathcal{E}_{km} = \begin{cases} -\mathcal{E}_{mk} & m=1,\dots,N \\ 0 & m=N+1,\dots,M \end{cases} \qquad (20)$$

then the above $\mathcal{E}^2$ term is $\emptyset$, and we need to look at the next expansion in Eq. (18).

$$E - \sum_{k=1}^{N} \epsilon_k = -\sum_{k,m=1}^{N} \epsilon_k \left(\sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im}\right)^2$$ note $\epsilon_{km} + \epsilon_{mk} = 0$ by the condition

$$- \sum_{k=1}^{N} \sum_{m=N+1}^{M} (\epsilon_k + \epsilon_m) \left(\sum_{i=1}^{N} \epsilon_{ik} \underbrace{\epsilon_{im}}_{\equiv \emptyset}\right)^2$$ note $\epsilon_{km} = 0$ by the condition

from the condition

$$- \sum_{k,m=N+1}^{M} \epsilon_k \left(\sum_{i=1}^{N} \underbrace{\epsilon_{ik}\epsilon_{im}}_{\equiv \emptyset}\right)^2$$

from the condition

$$\therefore E - \sum_{k=1}^{N} \epsilon_k = -\sum_{k,m=1}^{N} \overset{occ}{\epsilon_k} \left(\sum_{i=1}^{N} \epsilon_{ik}\epsilon_{im}\right)^2 \qquad (21)$$

This again is positive definite if and only if all the occupied states are negative. //