Density Matrix Minimization: Real-Space Basis

6/19/03

[E. Hernandez, M.J. Gillan, C.M. Goringe, PRB 53, 7147 ('96)]

— Energy functional

$$\Omega = \sum_i f_i \int dr\, \psi_i^*(r)(\hat{H}_r - \mu)\psi_i(r) \tag{1}$$

$$= \int dr \left[(\hat{H}_r - \mu) \sum_i f_i \psi_i(r)\psi_i^*(r')\right]_{r'\to r}$$

$$\therefore \Omega = \int dr \left[(\hat{H}_r - \mu)\rho(r,r')\right]_{r'\to r} \tag{2}$$

where

$$\rho(r,r') = \sum_i f_i \psi_i(r)\psi_i^*(r') \tag{3}$$

f_i is the Fermi distribution, $\{\psi_i(r)\}$ is the energy eigenstate set. We generalize Eq. (2) to a functional of general density matrix $\rho(r,r')$ with the following constraints:

(i) Normalization

$$N_e = \int dr\, \rho(r,r) \tag{4}$$

where N_e is the number of electrons.

(ii) Idempotency (at $T = 0$)

$$\int dr'\, \rho(r,r')\rho(r',r'') = \rho(r,r'') \tag{5}$$

☺ $\hat{\rho}^2 = \hat{\rho}$ (see 6/18/03)

$\langle r|\hat{\rho}\hat{\rho}|r''\rangle = \langle r|\hat{\rho}|r''\rangle$

$\int dr'|r'\rangle\langle r'| = I$ (☹ closure relation)

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- Separable trial function

We restrict the variational space to the following separable form:

→ ~~If this is diagonalized, SVD low-rank~~

$$\rho(r,r') = \sum_{\alpha\beta} \phi_\alpha(r)\, K_{\alpha\beta}\, \phi^*_\beta(r') \qquad (6)$$

↳ ab initio basis to be determined (KS-like)

where $\phi_\alpha(r)$ is a localized basis (support function). The index α collectively denotes the atom index i and basis orbitals μ per atom. ϕ_α are nonzero only inside spherical regions of radius R_{reg}.

$$\phi_\alpha(r) = 0 \qquad (|r - R_\alpha| > R_{reg}) \qquad (6)$$

where R_α is the position of atom α. (In DMDC, block size L_b becomes the corresponding parameter.)

— Density matrix purification

Given a trial density matrix

$$\sigma(r,r') = \sum_{\alpha\beta} \phi_\alpha(r)\, L_{\alpha\beta}\, \phi^*_\beta(r') \tag{7}$$

the purified density matrix, Eq. (6), is obtained as

$$\rho = 3\sigma * \sigma - 2\sigma * \sigma * \sigma \tag{8}$$

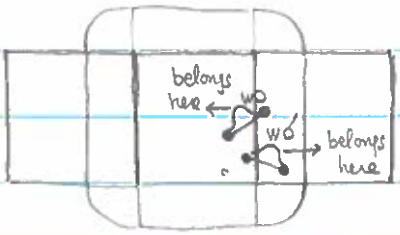
where $C = A * B$ is a short-hand notation for

$$C(r,r') = \int dr'' A(r,r'')\, B(r'',r') \tag{9}$$

※ Note that purification only applies to subspace rotation, $L \to K$, but not to the ab initio orbitals $\{\phi_\alpha(r)\}$, which is the same in the LCWO in DMDC.

↓ Redundancy-ill conditioning avaidance

DMDC recipe: Each block only keeps Wannier orbitals whose centers-of-mass ∈ region.



Substituting the separable trial form, Eq. (7), in (8),

$$\rho(1,2) = 3\int d3 \sum_{\alpha\beta} \phi_\alpha(1) L_{\alpha\beta} \phi^*_\beta(3) \sum_{\gamma\delta} \phi_\gamma(3) L_{\gamma\delta} \phi^*_\delta(2)$$

$$\rightarrow S_{\beta\gamma}$$

$$- 2\int d3 \int d4 \sum_{\alpha\beta} \phi_\alpha(1) L_{\alpha\beta} \phi^*_\beta(3) \sum_{\gamma\delta} \phi_\gamma(3) L_{\gamma\delta} \phi^*_\delta(4) \sum_{\eta\nu} \phi_\eta(4) L_{\eta\nu} \phi^*_\nu(2)$$

$$\hookrightarrow S_{\beta\gamma} \qquad \hookrightarrow S_{\delta\eta}$$

$$= 3 \sum_{\alpha\beta}\sum_{\gamma\delta} \phi_\alpha(1) L_{\alpha\beta} S_{\beta\gamma} L_{\gamma\delta} \phi^*_\delta(2)$$

$$- 2 \sum_{\alpha\beta}\sum_{\gamma\delta}\sum_{\eta\nu} \phi_\alpha(1) L_{\alpha\beta} S_{\beta\gamma} L_{\gamma\delta} S_{\delta\eta} L_{\eta\nu} \phi^*_\nu(2)$$

$$= 3 \sum_{\alpha\delta} \phi_\alpha(1) (LSL)_{\alpha\delta} \phi^*_\delta(2)$$

$$- 2 \sum_{\alpha\nu} \phi_\alpha(1) (LSLSL)_{\alpha\nu} \phi^*_\nu(2)$$

$$\therefore \rho(r,r') = \sum_{\alpha\beta} \phi_\alpha(r) \left(3LSL - 2LSLSL\right)_{\alpha\beta} \phi^*_\beta(r') \qquad (10)$$

where

$$S_{\alpha\beta} = \int dr\, \phi^*_\alpha(r) \phi_\beta(r') \qquad (11)$$

Comparison of Eqs. (6) and (10) yields

$$K = 3LSL - 2LSLSL \qquad (12)$$

(Local approximation)

$$L_{\alpha\beta} = 0 \qquad (|R_\alpha - R_\beta| > R_L) \qquad (13)$$

where R_L is the off-diagonal density matrix cut-off.

— Density-matrix minimization

The grand potential, Eq. (2), is minimized with respect to $L_{\alpha\beta}$ and $\phi_\alpha(r)$. For DMDC, only variation with respect to $L_{\alpha\beta}$ is relevant, since the ab initio Wannier orbitals $\phi_\alpha(r)$ are fixed in the first (divide-and-conquer) phase and their mesh-level variation is irrelevant (too fine grained) for the construction of global density matrix.

(Variation with respect to $K_{\alpha\beta}$)

We may take a two-phase approach:

Phase 1: McWeeny purification (fixed-point iteration) of DM

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for step = 1 to n_fp
    K ← 3KSK − 2KSKSK
endfor
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Phase 2: Energy minimization (greedy → conjugate gradient algorithm)

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for step = 1 to n_cg
    K ← K − τ ∂Ω/∂K
endfor
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Substitute the trial function, Eq.(6), in Eq. (2)

$$\Omega[\rho] = \int dr \sum_{\alpha\beta} \left[(\hat{H}_r - \mu)\, \phi_\alpha(r)\, K_{\alpha\beta}\, \phi^*_\beta(r') \right]_{r' \to r}$$

$$= \sum_{\alpha\beta} K_{\alpha\beta} \underbrace{\int dr\, \phi^*_\beta(r) (\hat{H}_r - \mu)\, \phi_\alpha(r)}_{H'_{\beta\alpha}}$$

$$\therefore \Omega[K] = \sum_{\alpha\beta} K_{\alpha\beta} H_{\beta\alpha} \tag{7}$$

where

$$H'_{\alpha\beta} = \int dr\, \phi^*_\beta(r) (\hat{H}_r - \mu)\, \phi_\alpha(r) \tag{8}$$

Taking the variation w.r.t. K,

$$\delta\Omega = \sum_{\alpha\beta} \delta K_{\alpha\beta} H'_{\beta\alpha} \equiv \sum_{\alpha\beta} \delta K_{\alpha\beta} \frac{\partial \Omega}{\partial K_{\alpha\beta}}$$

$$\therefore \frac{\partial \Omega}{\partial K_{\alpha\beta}} = H'_{\beta\alpha} \tag{9}$$