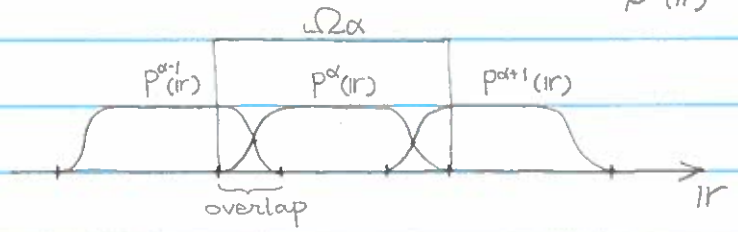
Divide-and-Conquer Density Functional Theory

6/3/03

[W. Yang, PRL 66, 1438 ('91); W. Yang & T.-S. Lee, JCP 103, 5674 ('95)]

— Spatial decomposition function (overlapping)

$$\begin{cases} \sum_\alpha p^\alpha(\mathbf{r}) = 1 & (1) \\ \rho(\mathbf{r}) = \left(\sum_\alpha p^\alpha(\mathbf{r})\right)\rho(\mathbf{r}) = \sum_\alpha \underbrace{p^\alpha(\mathbf{r})\rho(\mathbf{r})}_{\rho^\alpha(\mathbf{r})} = \sum_\alpha \rho^\alpha(\mathbf{r}) & (2) \end{cases}$$



(Example)

$$p^\alpha(\mathbf{r}) = \frac{\exp(-\lambda|\mathbf{r}-\mathbf{R}_\alpha|)}{\sum_\alpha \exp(-\lambda|\mathbf{r}-\mathbf{R}_\alpha|)} \quad (3)$$

The decomposed density $\rho^\alpha(\mathbf{r})$ can be expressed "exactly" as

$$\rho^\alpha(\mathbf{r}) = p^\alpha(\mathbf{r}) \langle \mathbf{r}| \frac{2}{\exp[\beta(\hat{H}-\mu)]+1} |\mathbf{r}\rangle \quad (4)$$

$\hat{H}$: Kohn-Sham Hamiltonian; μ: "global" chemical potential.

The chemical potential μ is determined by solving

$$N = \int d^3r\, \rho(\mathbf{r}) = \int d^3r \langle \mathbf{r}| \frac{2}{\exp[\beta(\hat{H}-\mu)]+1} |\mathbf{r}\rangle \quad (5)$$

- Crux of linear-scaling "approximation"

We now approximate Eq.(4) as

$$\rho^{\alpha}(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) \langle \mathbf{r}| \frac{2}{\exp[\beta(\hat{H}-\mu)]+1} |\mathbf{r}\rangle \simeq \rho^{\alpha} \langle \mathbf{r}| \frac{2}{\exp[\beta(\hat{H}^{\alpha}-\mu)+1} |\mathbf{r}\rangle \quad (6)$$

where (in atomic unit)

$$\hat{H}^{\alpha} = -\frac{1}{2}\nabla^2 + v_{ion}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + v_{xc}(\rho(\mathbf{r})) \Big|_{\mathbf{r}\in\Omega_{\alpha}} \quad (7)$$

Though $\mathbf{r}\in\Omega_{\alpha}$, $\forall \mathbf{r}\in \bigcup_{\alpha}\Omega_{\alpha}$ contribute to the Hartree potential. We may need to adopt Merz's dual-buffer divide-&-conquer scheme (see a separate note on 6/3/03).

— Divide-&-conquer algorithm

1. Solve the sub-space eigenvalue problem on each $\Omega_\alpha + \Delta_\alpha$. ($\Delta_\alpha$: buffer)

$$\hat{H}^\alpha |m\rangle = \epsilon_m |m\rangle \quad \text{occupied (\# not known)} + \alpha \tag{8}$$

2. $$\rho^\alpha(\mathbf{r}) = \sum_m P^\alpha(\mathbf{r}) \frac{2}{\exp[\beta(\epsilon_m - \mu)] + 1} |\psi_m(\mathbf{r})|^2 \tag{9}$$

3. Solve $N = \sum_\alpha \int d^3r \, \rho^\alpha(\mathbf{r})$ for μ

4. Compute $\rho(\mathbf{r}) = \sum_\alpha \rho^\alpha(\mathbf{r}) \longrightarrow v_H(\mathbf{r}) + v_{XC}(\mathbf{r})$ in $\forall \Omega_\alpha$

5. If not converged, go to 1.

Density-Matrix Divide-and-Conquer

6/4/03

[W. Yang & T.-S. Lee, JCP 103, 5674 ('95)]

— Objectives

① Finite-difference divide-and-conquer (FDDC)
Replace the Wannier/atomic orbitals: $i \rightarrow \mathbf{r}$

② Initialize FDDC with non-orthogonal-Wannier/SVD (NOW/SVD) convergence aid.

— Key

① Introduction of Wannier/atomic basis

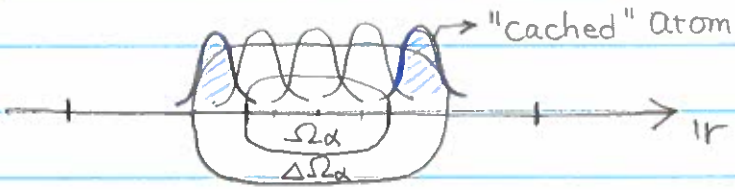
② 1-1/2-0 density-matrix partition

— Subsystem partition / augmentation

1. Partition the physical space into disjoint subspaces $\{\Omega_\alpha\}$.

2. For each subsystem Ω_α, define non-orthogonal, local basis functions $\{\phi_i^\alpha(\mathbf{r})\}$.

3. Augment each subsystem Ω_α with a skin layer $\Delta\Omega_\alpha$, the basis functions in which overlap with those in Ω_α; augment basis-function to $\{\phi_i^\alpha(\mathbf{r}) \mid i \in \Omega_\alpha + \Delta\Omega_\alpha\}$.



※ The "cached" atomic basis functions are analogous to the cached atoms in spatial-decomposed MD.

4. (Augmented) local Hamiltonian

$$\hat{H}_\alpha \equiv \hat{H} \text{ spanned by } \{\phi_i(\mathbf{r})\} \in \Omega_\alpha + \Delta\Omega_\alpha \tag{1}$$

$$= \{ \langle i|\hat{H}|j\rangle \mid i,j \in \Omega_\alpha + \Delta\Omega_\alpha \} \tag{2}$$

The local eigenvalue problem is represented as

$$\hat{H}\mathcal{P}_\alpha |m\rangle = \epsilon_m \mathcal{P}_\alpha |m\rangle \tag{3}$$

where we restrict the eigenvector to a low-rank space spanned by the projection operator

$$\mathcal{P}_\alpha = \sum_{i\in\Omega_\alpha+\Delta\Omega_\alpha} |i\rangle\langle i| \tag{4}$$

$\langle i| \times$ Eq. (3)

$$\langle i|\hat{H} \sum_{j\in\Omega_\alpha+\Delta\Omega_\alpha} |j\rangle\langle j|m\rangle = \sum_{j\in\Omega_\alpha+\Delta\Omega_\alpha} \langle i|j\rangle\langle j|m\rangle \epsilon_m$$

$$\sum_j \underbrace{\langle i|\hat{H}|j\rangle}_{H^\alpha_{ij}} \underbrace{\langle j|m\rangle}_{C^\alpha_{jm}} = \sum_j \underbrace{\langle i|j\rangle}_{S^\alpha_{ij}} \underbrace{\langle j|m\rangle}_{C^\alpha_{jm}} \epsilon_m$$

(Augmented local eigenvalue problem in $\Omega_\alpha + \Delta\Omega_\alpha$)

$$\mathbb{H}^\alpha \mathbb{C}^\alpha = \mathbb{S}^\alpha \mathbb{C}^\alpha \mathbb{E}^\alpha \tag{5}$$

where all matrices are defined for $i,j \in \Omega_\alpha + \Delta\Omega_\alpha$.

$$H^\alpha_{ij} = \langle i|H|j\rangle \tag{6}$$

$$C^\alpha_{jm} = \langle j|m\rangle \tag{7}$$

$$S^\alpha_{ij} = \langle i|j\rangle \tag{8}$$

$$\mathbb{E}^\alpha = \mathrm{diag}(\epsilon_1, \epsilon_2, \ldots, \epsilon_M) \tag{9}$$

※ Since no filtering is applied, $\mathbb{S}^\alpha$ is in general not singular. Otherwise, SVD of $\mathbb{S}^\alpha$ is used to extract $\tilde{M} < M$ eigenstates.

— Spatial decomposition of density matrix

The density matrix $\rho(\mathbf{r},\mathbf{r}')$ of the entire system is defined as

$$\rho(\mathbf{r},\mathbf{r}') = 2\sum_m \psi_m(\mathbf{r}) \frac{1}{\exp[\beta(\epsilon_m-\mu)]+1} \psi_m^*(\mathbf{r}') \tag{10}$$

$$= \sum_{ij} \rho_{ij} \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}') \tag{11}$$

where $\psi_m(\mathbf{r}) = \langle \mathbf{r}|m\rangle$ (without $\mathcal{P}_\alpha$ projection).

Note that

$$\psi_m(\mathbf{r}) = \sum_i \phi_i(\mathbf{r}) \langle i|m\rangle = \sum_i \phi_i(\mathbf{r}) C_{im} \tag{12}$$

Substituting Eq.(12) in (10),

$$\rho(\mathbf{r},\mathbf{r}') = 2\sum_m \sum_i \phi_i(\mathbf{r}) C_{im} \frac{1}{\exp[\beta(\epsilon_m-\mu)]+1} \sum_j C_{jm}^* \phi_j^*(\mathbf{r})$$

$$= \sum_{ij} \phi_i(\mathbf{r}) \left[2\sum_m \frac{C_{im} C_{jm}^*}{\exp[\beta(\epsilon_m-\mu)]+1} \right] \phi_j^*(\mathbf{r})$$

Comparing this with Eq.(11)

$$\rho_{ij} = 2\sum_m \frac{C_{im} C_{jm}^*}{\exp[\beta(\epsilon_m-\mu)]+1} \tag{13}$$

We introduce spatial-decomposition support functions as

$$P_{ij}^{\alpha} = \begin{cases} 1 & i,j \in \alpha \\ 1/2 & i \in \alpha, j \notin \alpha \quad \vee \quad i \notin \alpha, j \in \alpha \\ \varnothing & i,j \notin \alpha \end{cases} \tag{14}$$

so that

$$\sum_{\alpha} P_{ij}^{\alpha} = 1 \tag{15}$$

The partitioned density-matrices are introduced as

$$\rho_{ij} = \left(\sum_{\alpha} P_{ij}^{\alpha}\right) \rho_{ij} = \sum_{\alpha} \left(P_{ij}^{\alpha} \rho_{ij}\right) = \sum_{\alpha} \rho_{ij}^{\alpha} \tag{16}$$

where

$$\rho_{ij}^{\alpha} = P_{ij}^{\alpha} \rho_{ij} \tag{17}$$

— Divide-and-conquer approximation

Substituting Eq. (13) in (17),

$$\rho_{ij}^{\alpha} = P_{ij}^{\alpha} \, 2 \sum_{m} \frac{C_{im} C_{jm}^{*}}{\exp[\beta(\epsilon_m - \mu)] + 1}$$

$$\simeq P_{ij}^{\alpha} \, 2 \sum_{m} \frac{C_{im} C_{jm}^{*}}{\exp[\beta(\epsilon_m^{\alpha} - \mu)] + 1} \tag{18}$$

This apparently innocent approximation, $\epsilon_m \simeq \epsilon_m^{\alpha}$, is the crux of linear scaling:

Instead of solving $\mathbb{H}\mathbb{C} = \mathbb{S}\mathbb{C}\mathbb{E}$ in the entire space. to obtain $\{\epsilon_m\}$

↓

Solve $\mathbb{H}^{\alpha}\mathbb{C}^{\alpha} = \mathbb{S}^{\alpha}\mathbb{C}^{\alpha}\mathbb{E}^{\alpha}$ independently to obtain $\{\epsilon_m^{\alpha}\}$.

– Chemical potential equalization

$$N = \int d\mathbf{r}\, \rho(\mathbf{r},\mathbf{r}) \tag{19}$$

$$= \int d\mathbf{r} \sum_{i,j} P_{ij} \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r})$$

$$= \sum_{i,j} P_{ij} \int d\mathbf{r} \underbrace{\phi_j^*(\mathbf{r}) \phi_i(\mathbf{r})}_{\langle j|\mathbf{r}\rangle\langle \mathbf{r}|i\rangle}$$

$$\langle j|i\rangle = S_{ji}$$

$$\therefore N = \sum_{i,j} P_{ij} S_{ji} \tag{20}$$

where N is the number of total electrons.

Substituting Eq. (13) to (20)

$$N = \sum_{i,j} 2 \sum_m \frac{C_{im} C_{jm}^*}{\exp[\beta(\epsilon_m - \mu)] + 1} S_{ji} \tag{21}$$

(Divide-and-conquer approximation

$\sum_\alpha P_\alpha \times$ (21)

$$N = \sum_\alpha \sum_{i,j} P_{ij}^\alpha \, 2 \sum_m \frac{C_{im} C_{jm}^*}{\exp[\beta(\epsilon_m - \mu)] + 1} S_{ji}$$

$$\simeq \sum_\alpha \left[2 \sum_{i,j} P_{ij}^\alpha \sum_m \frac{C_{im} C_{jm}^*}{\exp[\beta(\epsilon_m^\alpha - \mu)] + 1} S_{ji} \right]$$

Note that

$$P_{ij}^\alpha S_{ji} \neq 0 \quad \text{if} \quad \neg(i,j \notin \alpha)$$

$$\therefore P_{ij}^\alpha S_{ji} = P_{ij}^\alpha S_{ji}{}^\alpha \tag{22}$$

$$\therefore N \simeq \sum_{\alpha} \left[2 \sum_{i,j} P_{ij}^{\alpha} \sum_{m} \frac{C_{im} C_{jm}^{*}}{\exp[\beta(\epsilon_m - \mu)] + 1} S_{ji}^{\alpha} \right] \tag{23}$$

– Density-matrix divide-and-conquer algorithm.

① Solve the augmented local eigenvalue problems

$$\mathbb{H}^{\alpha} \mathbb{C}^{\alpha} = \mathbb{S}^{\alpha} \mathbb{C}^{\alpha} \mathbb{E}^{\alpha} \quad \in \Omega_{\alpha} + \Delta\Omega_{\alpha} \text{ for } \forall \alpha \text{ independently}$$

② Determine the chemical potential μ by solving

$$N = \sum_{\alpha} \left[2 \sum_{i,j} P_{ij}^{\alpha} \frac{C_{im}^{\alpha} C_{jm}^{\alpha *}}{\exp[\beta(\epsilon_m^{\alpha} - \mu)] + 1} S_{ji}^{\alpha} \right]$$