Density Functional Theory with Nonorthogonal Orbitals

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– DFT with orthogonal orbitals — constrained minimization

(Problem) Minimize the energy functional,

$$E[\{\psi_i(\mathbf{r})\}] = \sum_{i=1}^{N} \langle \psi_i | \frac{\hat{p}^2}{2m} | \psi_i \rangle + F[\rho(\mathbf{r})] \qquad (1)$$

with the orthonormal constraints,

$$\langle \psi_i | \psi_j \rangle = \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij} \qquad (2)$$

In Eq. (1),

$$\begin{cases} \rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 & (3) \\ F[\rho(\mathbf{r})] = \int d\mathbf{r}\, \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + F_{xc}[\rho(\mathbf{r})] & (4) \end{cases}$$

Note that

$$\langle \psi_i | \frac{\hat{p}^2}{2m} | \psi_i \rangle = \int d\mathbf{r}\, \underbrace{\langle \psi_i | \mathbf{r} \rangle}_{\psi_i^*(\mathbf{r})} \underbrace{\langle \mathbf{r} | \frac{\hat{p}^2}{2m} \psi_i \rangle}_{-\frac{\hbar^2 \nabla^2}{2m} \langle \mathbf{r} | \psi_i \rangle = -\frac{\hbar^2 \nabla^2}{2m} \psi_i(\mathbf{r})} = \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \psi_i(\mathbf{r}) \qquad (5)$$

(☺ 12/31/99)

– Constrained minimization procedure

(Gradient)

$\psi_i(\mathbf{r})$ and $\psi_i^*(\mathbf{r})$ are taken to be independent functions.

$$\frac{\delta E}{\delta \psi_i^*(\mathbf{r})} = -\frac{\hbar^2}{2m}\nabla^2 \psi_i(\mathbf{r}) + \int d\mathbf{r}' \underbrace{\frac{\delta \rho(\mathbf{r}')}{\delta \psi_i^*(\mathbf{r})}}_{\psi_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')} \frac{\delta F}{\delta \rho(\mathbf{r}')}$$

(☺ functional chain rule)

$$= -\frac{\hbar^2}{2m}\nabla^2 \psi_i(\mathbf{r}) + \underbrace{\frac{\delta F}{\delta \rho(\mathbf{r})}}_{v_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta F_{xc}}{\delta \rho(\mathbf{r})}} \psi_i(\mathbf{r})$$

$$\therefore \frac{\delta E}{\delta \psi_i^*(\mathbf{r})} = h(\mathbf{r})\,\psi_i(\mathbf{r})$$

$$= \Big[-\frac{\hbar^2}{2m}\nabla^2 + \underbrace{v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})}_{v(\mathbf{r})}\Big]\psi_i(\mathbf{r}) \tag{6}$$

where

$$v_H(\mathbf{r}) = e^2\int d\mathbf{r}'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \text{(Hartree potential)} \tag{7}$$

$$v_{xc}(\mathbf{r}) = \frac{\delta F_{xc}}{\delta \rho(\mathbf{r})} \quad \text{(exchange-correlation potential)} \tag{8}$$

(Lagrange multiplier)

Minimize, without constraint,

$$\tilde{E}[\{\psi_i(\mathbf{r})\}] = E[\{\psi_i(\mathbf{r})\}] - \sum_{ij}\Lambda_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij}) \tag{9}$$

The gradient is

$$g_i \equiv -\frac{\partial \tilde{E}}{\partial \psi_i^*(\mathbf{r})} \tag{10}$$

$$= -h(\mathbf{r})\,\psi_i(\mathbf{r}) + \sum_j \Lambda_{ij}\,\psi_j(\mathbf{r}) \tag{11}$$

The Lagrange multipliers, Λ_{ij}, are determined to satisfy the orthonormal constraints (e.g., using SHAKE-like iterative procedures).

Often the orthonormal constraints are satisfied by Gram-Schmidt procedures, not through the constraint forces except for the diagonal ones. Diagonal constraint forces are derived considering the fallowing unconstrained functional.

$$e[\psi_i(\mathbf{r})] = \frac{\langle\psi_i|h|\psi_i\rangle}{\langle\psi_i|\psi_i\rangle} \tag{12}$$

$$\frac{\delta e}{\delta\psi_i^*(\mathbf{r})} = \frac{h|\psi_i\rangle}{\langle\psi_i|\psi_i\rangle} - \frac{\langle\psi_i|h|\psi_i\rangle}{\langle\psi_i|\psi_i\rangle^2}|\psi_i\rangle$$

$$\xrightarrow[\langle\psi_i|\psi_i\rangle=1]{} (h - \langle\psi_i|h|\psi_i\rangle)|\psi_i\rangle \tag{13}$$

(Oridinary procedure)

① Use an iterative method such as conjugate gradient using gradients,

$$\begin{cases} g_i = -[h(\mathbf{r}) - \epsilon_i]\psi_i(\mathbf{r}) & (14) \\ \epsilon_i = \langle\psi_i|h|\psi_i\rangle & (15) \end{cases}$$

② After each iterative step, reinforce the orthonormal constraints by the Gram-Schmidt procedure,

$$|\psi_i\rangle \longleftarrow |\psi_i\rangle - \sum_{j<i}|\psi_j\rangle\langle\psi_j|\psi_i\rangle \tag{16}$$

Note that

$$\hat{Q} \equiv \mathbb{1} - \sum_{j<i}|\psi_j\rangle\langle\psi_j| \tag{17}$$

is the projection operator "out of" the subspace spanned by $\{|\psi_j\rangle | j<i\}$, i.e., the lower-lying states.

Biorthogonal compliment

[E.B. Stechel, A.R. Williams, & P.J. Feibelman, PRB 49, 10088 ('94)]

Consider a finite Hilbert space $\mathcal{H}$ of dimension N, spanned by a linearly independent set $\{\phi_i \mid i = 1, 2, \ldots, N\}$. The "metric" of the (curved) space is defined by the overlap matrix $\mathbb{S}$,

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{18}$$

The biorthogonal compliment is defined as the set $\{\bar{\Phi}_i \mid i = 1, 2, \ldots, N\}$, where

$$|\bar{\Phi}_i\rangle = \sum_{j=1}^{N} |\phi_j\rangle S^{-1}_{ji} \tag{19}$$

The biorthogonal compliment satisfies the biorthogonality relationship,

$$\langle \bar{\Phi}_i | \phi_j \rangle = \delta_{ij} \tag{20}$$

$$\left(∵ \ \langle \bar{\Phi}_i | \phi_j \rangle = \sum_k \underbrace{(S^{-1}_{ki})^*}_{S^{-1}_{ik}} \underbrace{\langle \phi_k | \phi_j \rangle}_{S_{kj}} = \delta_{ij} \ // \right)$$

Note that <u>S_{ij} is Hermitian</u>,

$$S^*_{ij} = \langle \psi_i | \psi_j \rangle^* = \langle \psi_j | \psi_i \rangle = S_{ji} \tag{21}$$

On $\mathcal{H}$, the unit operator is defined as

$$\mathbb{1} = \sum_{i=1}^{N} |\bar{\Phi}_i\rangle \langle \phi_i | \tag{22}$$

$$\left(∵ \ \left[\sum_i |\bar{\Phi}_i\rangle \langle \phi_i|\right] |\phi_j\rangle = \sum_i \sum_k |\phi_k\rangle S^{-1}_{ki} \underbrace{\langle \phi_i | \phi_j \rangle}_{S_{ij}} = \sum_k |\phi_k\rangle \delta_{kj} = |\phi_j\rangle \ // \right)$$

$$\boxed{\langle \bar{\phi}_i | = \sum_j (S^{-1}_{ji})^* \langle \phi_j | = \sum_j S^{-1}_{ij} \langle \phi_j |} \quad (5)$$

Biorthogonal energy functional

All relevant quantities (if a fully separable pseudopotential is used — G. Galli & M. Parrinello, PRL 69, 3547 ('92) — check!) for DFT (single-particle scheme) depend on $\bar{\phi}_i^*(\mathbf{r})\, \phi_i(\mathbf{r})$. The energy functional is,

$$E[\{\phi_i(\mathbf{r})\}] = \sum_i \langle \bar{\phi}_i | \frac{\hat{p}^2}{2m} | \phi_i \rangle + F[\rho(\mathbf{r})] \quad (23)$$

$$= \sum_i \sum_j S^{-1}_{ij} \langle \phi_j | \frac{\hat{p}^2}{2m} | \phi_i \rangle + F[\rho(\mathbf{r})] \quad (24)$$

$$\rho(\mathbf{r}) = \sum_i \bar{\phi}_i^*(\mathbf{r})\, \phi_i(\mathbf{r}) \quad (25)$$

$$= \sum_i \sum_j S^{-1}_{ij}\, \phi_j^*(\mathbf{r})\, \phi_i(\mathbf{r}) \quad (26)$$

Eqs. (23) – (26) are equivalent to Eqs. (1) and (3) by introducing the orthonormal set defined by

$$|\psi_i\rangle = \sum_j |\phi_j\rangle S^{-1/2}_{ji} \quad (27)$$

(Orthonormality)

$$\langle \psi_i | \psi_j \rangle = \sum_k \underbrace{(S^{-1/2}_{ki})^*}_{S^{1/2}_{ik}} \langle \phi_k | \left(\sum_l |\phi_l\rangle S^{-1/2}_{lj} \right)$$

$$= \sum_l \left(\sum_k S^{-1/2}_{ik} S_{kl} \right) S^{-1/2}_{lj}$$

$$= \sum_l S^{1/2}_{il} S^{-1/2}_{lj}$$

$$= \delta_{ij} \quad (28)$$

The orthonormal density functional is

① $$E[\{\psi_i(\mathbf{r})\}] = \sum_{i=1}^{N} \langle \psi_i | \frac{\hat{p}^2}{2m} | \psi_i \rangle + F[\rho(\mathbf{r})]$$

$$= \sum_i \sum_j S_{ij}^{-1/2} \langle \phi_j | \frac{\hat{p}^2}{2m} \left(\sum_k |\phi_k\rangle S_{ki}^{-1/2} \right) + F[\rho(\mathbf{r})]$$

$$= \sum_{jk} \underbrace{\left(\sum_k S_{ki}^{-1/2} S_{ij}^{-1/2} \right)}_{S_{kj}^{-1}} \langle \phi_j | \frac{\hat{p}^2}{2m} | \phi_k \rangle + F[\rho(\mathbf{r})] = \text{Eq. (24)}$$

② $$\rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

$$= \sum_i \sum_j \phi_j^*(\mathbf{r}) \underbrace{(S_{ji}^{-1/2})^*}_{S_{ij}^{-1/2}} \sum_k \phi_k(\mathbf{r}) S_{ki}^{-1/2}$$

$$= \sum_{jk} \underbrace{\left(\sum_i S_{ki}^{-1/2} S_{ij}^{-1/2} \right)}_{S_{kj}^{-1}} \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r})$$

$$= \sum_{jk} S_{kj}^{-1} \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r}) = \text{Eq. (26)}$$

The equivalence ① and ② proves that Eqs. (24) and (26) are proper functionals to be minimized without constraints.