Auxiliary-Field Conjugate-Gradient Calculation of Electronic Structures in Density Functional Theory

5/27/92

§. Kohn-Sham Scheme

$$E[\{\psi_i(\mathbb{r})\}] = \sum_i \int d\mathbb{r}\, \psi_i^*(\mathbb{r})\left(-\frac{\hbar^2}{2m_*}\nabla^2\right)\psi_i(\mathbb{r}) + \int d\mathbb{r}\, n(\mathbb{r})\, v_{ext}(\mathbb{r})$$

$$+ \frac{1}{2}\int d\mathbb{r}\, n(\mathbb{r})\, v_H(\mathbb{r}) + E_{xc}[n(\mathbb{r})] \qquad (1)$$

$$\begin{cases} n(\mathbb{r}) = \sum_i |\psi_i(\mathbb{r})|^2 & (2) \\ \nabla^2 v_H(\mathbb{r}) = -\dfrac{4\pi e^2}{\epsilon} n(\mathbb{r}) \quad \text{(with a proper boundary condition)} & (3) \end{cases}$$

In the Kohn-Sham scheme, we minimize the energy functional, Eq. (1), with constraints,

$$\int d\mathbb{r}\, \psi_i^*(\mathbb{r})\, \psi_j(\mathbb{r}) = \delta_{ij} \qquad (4)$$

With a boundary condition where the Hartree field due to a point charge becomes zero at infinty, we can solve the Hartree field as

$$v_H(\mathbb{r}) = \int d\mathbb{r}' \frac{e^2}{\epsilon|\mathbb{r}-\mathbb{r}'|} n(\mathbb{r}') \qquad (5)$$

(Eular-Lagrange Equation)

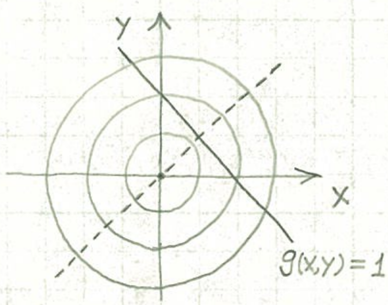
We minimize Eq. (1) with respect to $\psi_i(\mathbb{r})$ with constraints, Eq. (4), and using the Hartree field, Eq. (5),

$$\boxed{\frac{\delta}{\delta\psi_i^*(\mathbb{r})}\left\{E[\{\psi_i(\mathbb{r})\}] - \sum_{ij}\lambda_{ij}\left[\int d\mathbb{r}\,\psi_i^*(\mathbb{r})\psi_j(\mathbb{r}) - \delta_{ij}\right]\right\} = 0 \qquad (6)}$$

where λ_{ij} are Lagrange multipliers.

(example: Lagrange multiplier method)

Minimize $f(x,y) = x^2+y^2$ with a constraint $g(x,y) = x+y = 1$.



We instead minimize

$$h_\lambda(x,y) = f(x,y) - \lambda\, g(x,y)$$

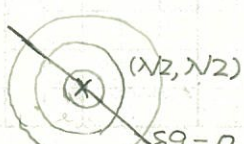
i.e.,

$$\begin{cases} \partial h_\lambda/\partial x = 2x - \lambda = 0 \\ \partial h_\lambda/\partial y = 2y - \lambda = 0 \end{cases} \rightarrow (x,y) = (\lambda/2, \lambda/2)$$

Let $(\delta x, \delta y)$ be an arbitrary displacement around $(\lambda/2, \lambda/2)$, then

$$\delta h_\lambda = \delta f - \lambda\,\delta g = 0 \quad \text{at } (\lambda/2, \lambda/2) \text{ for } \forall(\delta x, \delta y)$$

In particular, for a change which satisfies $\delta g = \delta x + \delta y = 0$, i.e., $(\delta x, -\delta x)$, $\delta h_\lambda = \delta f = 0$.



If we choose $\lambda = 1$, then $(1/2, 1/2)$ is a point around which $\forall h_1(1/2+\delta x, 1/2+\delta y) = f(1/2+\delta x, 1/2+\delta y) - g(1/2+\delta x, 1/2+\delta y)$ is larger than $h_1(1/2, 1/2)$, including the direction $(\delta x, -\delta x)$ where $g(1/2+\delta x, 1/2-\delta x) = 1$ is always satisfied.

Substituting Eq. (1) in (6),

$$-\frac{\hbar^2}{2m_*}\nabla^2 \psi_i(\mathbf{r}) + v_{ext}(\mathbf{r})\psi_i(\mathbf{r}) + \underbrace{\frac{\delta}{\delta\psi_i^*(\mathbf{r})}\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{e^2}{\epsilon|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r})n(\mathbf{r}') + \frac{\delta E_x}{\delta\psi_i^*(\mathbf{r})}}_{\int d\mathbf{r}'' \underbrace{\frac{\delta n(\mathbf{r}')}{\delta\psi_i^*(\mathbf{r})}}_{\delta(\mathbf{r}-\mathbf{r}')\psi_i(\mathbf{r})}\frac{\delta}{\delta n(\mathbf{r}')}\left[\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{e^2}{\epsilon|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r})n(\mathbf{r}') + E_{xc}\right]}$$

$$= \left[\int d\mathbf{r}'\frac{e^2}{\epsilon|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}') + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}\right]\psi_i(\mathbf{r})$$

$$-\sum_j \lambda_{ij}\psi_j(\mathbf{r}) = 0$$

$$\underbrace{\left[-\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext} + \int d\mathbf{r}'\frac{e^2}{\epsilon|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}') + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}\right]}_{h(\mathbf{r})}\psi_i(\mathbf{r}) = \sum_j \lambda_{ij}\psi_j(\mathbf{r}) \qquad (7)$$

$\int d\mathbf{r}\, \psi_k^*(\mathbf{r}) \times$ Eq. (7)

$$\langle k|h|i\rangle = \lambda_{ik} \qquad (8)$$

After getting an orthonormal set, $\{\psi_i(\mathbf{r}) \mid i = 1, \ldots, N\}$, which satisfy Eqs. (7) and (4), we can diagonalize the sub-space

Hamiltonian, Eq. (8).

$$\begin{bmatrix} h_{11} & \cdots & h_{1N} \\ \vdots & & \\ h_{N1} & \cdots & h_{NN} \end{bmatrix} \left[\begin{array}{c|c|c} u_1^{(1)} & & u_1^{(N)} \\ \vdots & \cdots & \vdots \\ u_N^{(1)} & & u_N^{(N)} \end{array}\right] = \left[\begin{array}{c|c|c} \epsilon^{(1)} u_1^{(1)} & & \epsilon^{(N)} u_1^{(N)} \\ \vdots & \cdots & \\ \epsilon^{(1)} u_N^{(1)} & & \epsilon^{(N)} u_N^{(N)} \end{array}\right] = \left[\begin{array}{c|c|c} u_1^{(1)} & & u_1^{(N)} \\ \vdots & \cdots & \vdots \\ u_N^{(1)} & & u_N^{(N)} \end{array}\right] \begin{bmatrix} \epsilon^{(1)} & & \\ & \ddots & \\ & & \epsilon^{(N)} \end{bmatrix} \tag{9}$$

i.e.,

$$\sum_k h_{ik} u_k^{(j)} = \epsilon^{(j)} u_i^{(j)} = \sum_k u_i^{(k)} [\epsilon^{(k)} \delta_{kj}] \tag{10}$$

Since h_{ik} is Hermitian, $\epsilon^{(j)}$ are real & $u_i^{(k)}$ can be unitary. Then, with a new set

$$\{ \varphi_i(\mathbf{r}) = \sum_j u_j^{(i)} \psi_j(\mathbf{r}) \mid i = 1, \ldots, N \}, \tag{11}$$

$$h(\mathbf{r}) \varphi_i(\mathbf{r}) = \sum_j \underbrace{h(\mathbf{r}) u_j^{(i)} \psi_j(\mathbf{r})}_{\sum_k h_{kj} \psi_k(\mathbf{r})}$$

$$= \sum_{jk} h_{kj} u_j^{(i)} \psi_k(\mathbf{r})$$

$$= \sum_k \epsilon^{(i)} u_k^{(i)} \psi_k(\mathbf{r}) = \epsilon^{(i)} \varphi_i(\mathbf{r}) \tag{12}$$

Also, note that

① $$\sum_i |\varphi_i(\mathbf{r})|^2 = \sum_{ijk} \underbrace{u_j^{(i)*}}_{u^{\dagger(j)}_i} \psi_j^*(\mathbf{r}) u_k^{(i)} \psi_k(\mathbf{r})$$

$$= \sum_{jk} \delta_{jk} \psi_j^*(\mathbf{r}) \psi_k(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \tag{13}$$

② $$\int d\mathbf{r}\, \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) = \sum_{kl} \underbrace{u_k^{*(i)}}_{u^{\dagger k}_{(i)}} u_l^{(j)} \underbrace{\int d\mathbf{r}\, \psi_k^*(\mathbf{r}) \psi_l(\mathbf{r})}_{\delta_{kl}}$$

$$= \sum_k u^{\dagger k}_{(i)} u_k^{(i)} = \delta_{ij} \tag{14}$$

We can rewrite the Eular-Lagrange equation as

$$\left[-\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon^{(i)}\varphi_i(\mathbf{r}) \tag{15}$$

$$\begin{cases} v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2}{\epsilon|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}') & (16) \\ n(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2 & (17) \\ v_{xc}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} E_{xc} & (18) \end{cases}$$

with constraints

$$\int d\mathbf{r}\, \varphi_i^*(\mathbf{r})\, \varphi_j(\mathbf{r}) = \delta_{ij} \tag{19}$$

§. Auxiliary-Field Formulation

$$E[\{\psi_i(\mathbb{r})\}, v_H(\mathbb{r})] = \sum_i \int d\mathbb{r}\, \psi_i(\mathbb{r}) \left(-\frac{\hbar^2}{2m_*}\nabla^2\right) \psi_i(\mathbb{r}) + \int d\mathbb{r}\, n(\mathbb{r})\, v_{ext}(\mathbb{r}) + E_{xc}[n(\mathbb{r})]$$
$$+ \frac{\epsilon}{8\pi e^2}\int d\mathbb{r}\, v_H(\mathbb{r}) \nabla^2 v_H(\mathbb{r}) + \int d\mathbb{r}\, n(\mathbb{r})\, v_H(\mathbb{r}) \qquad (20)$$

Minimize the energy functional, Eq. (20), with respect to $\psi_i(\mathbb{r})$ and an auxiliary field $v_H(\mathbb{r})$, with constraints,

$$\int d\mathbb{r}\ \psi_i^*(\mathbb{r})\, \psi_j(\mathbb{r}) = \delta_{ij} \qquad (21)$$

The Eular-Lagrange equations are

$$① \ \frac{\delta}{\delta\psi_i^*(\mathbb{r})}\left\{ E[\{\psi_i(\mathbb{r})\}, v_H(\mathbb{r})] - \sum_{ij} \lambda_{ij} \left[\int d\mathbb{r}\, \psi_i^*(\mathbb{r})\, \psi_j(\mathbb{r}) - \delta_{ij}\right] \right\} = 0 \qquad (22)$$

$$② \ \frac{\delta}{\delta v_H(\mathbb{r})} E[\{\psi_i(\mathbb{r})\}, v_H(\mathbb{r})] = 0 \qquad (23)$$

(Eular-Lagrange Equations for $\psi_i(\mathbf{r})$)

$$0 = -\frac{\hbar^2}{2m_*}\nabla^2\psi_i(\mathbf{r}) + v_{ext}(\mathbf{r})\psi_i(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}\psi_i(\mathbf{r}) + v_H(\mathbf{r})\psi_i(\mathbf{r}) - \sum_j \lambda_{ij}\psi_j(\mathbf{r}) \tag{24}$$

$\int d\mathbf{r}\, \psi_k^*(\mathbf{r}) \times$ Eq. (24) using Eq. (21)

$$\int d\mathbf{r}\, \psi_k^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_H(\mathbf{r})\right]\psi_i(\mathbf{r}) = \lambda_{ik} \tag{25}$$

$$\therefore \underbrace{\left[-\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]}_{h(\mathbf{r})}\psi_i(\mathbf{r}) = \sum_j \lambda_{ij}\psi_j(\mathbf{r}) \tag{26}$$

where

$$\lambda_{ij} = \int d\mathbf{r}\, \psi_j^*(\mathbf{r})\, h(\mathbf{r})\, \psi_i(\mathbf{r}) = \langle j|h|i\rangle \tag{27}$$

Or we can perform a subspace diagonalization of $\langle i|h|j\rangle$, so that

$$\left[-\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i\,\varphi_i(\mathbf{r}) \tag{28}$$

where

$$\epsilon_i = \int d\mathbf{r}\, \varphi_i^*(\mathbf{r})\, h(\mathbf{r})\, \varphi_i(\mathbf{r}) = \langle i|h|i\rangle \tag{29}$$

(Eular - Lagrange Equation for $v_H(\mathbf{r})$)

$$0 = \frac{\epsilon}{8\pi e^2} \int d\mathbf{r}' \left[\delta(\mathbf{r}'-\mathbf{r}) \nabla^2 v_H(\mathbf{r}') + v_H(\mathbf{r}') \nabla^2 \delta(\mathbf{r}'-\mathbf{r}) \right] + n(\mathbf{r})$$

$$= \frac{\epsilon}{8\pi e^2} \nabla^2 v_H(\mathbf{r}) \underbrace{- \frac{\epsilon}{8\pi e^2} \int d\mathbf{r}' \nabla v_H(\mathbf{r}') \cdot \nabla \delta(\mathbf{r}'-\mathbf{r})}_{+ \frac{\epsilon}{8\pi e^2} \int d\mathbf{r}' \nabla^2 v_H(\mathbf{r}') \delta(\mathbf{r}'-\mathbf{r})} + n(\mathbf{r})$$

$$= \frac{\epsilon}{4\pi e^2} \nabla^2 v_H(\mathbf{r}) + n(\mathbf{r})$$

$$\boxed{\therefore \quad \nabla^2 v_H(\mathbf{r}) = - \frac{4\pi e^2}{\epsilon} n(\mathbf{r}) \qquad (30)}$$

§. Gradient w.r.t. $\psi_i(\mathbf{r})$

To deal with the orthonormality condition, it is convenient to express the problem in terms of non-orthonormal set $\{\varphi_i(\mathbf{r})\}$ which is related to the orthonormal set $\{\psi_i(\mathbf{r})\}$ as

$$\psi_i = \sum_j S_{ij}^{-1/2} \varphi_j \tag{31}$$

where

$$S_{ij} = \int d\mathbf{r}\, \varphi_j^*(\mathbf{r})\, \varphi_i(\mathbf{r}) = \langle \varphi_j | \varphi_i \rangle \tag{32}$$

☺ Note that $S_{ij}^* = \langle \varphi_i | \varphi_j \rangle = S_{ji}$ (**unitary**), so is $S^{1/2}$.

$$\langle \psi_i | \psi_j \rangle = \sum_{kl} \underbrace{S_{ik}^{*-1/2}}_{S_{ki}^{-1/2}} S_{jl}^{-1/2} \underbrace{\langle \varphi_k | \varphi_l \rangle}_{S_{lk}}$$

$$= \sum_{kl} S_{jl}^{-1/2} S_{lk} S_{ki}^{-1/2} = \delta_{ji} \quad //$$

Energy functional Eq. (20) for $\{\psi_i(\mathbf{r})\}$ can be written as

$$E = \sum_i \int d\mathbf{r}\, \underbrace{\psi_i^*(\mathbf{r})}_{\sum_j S_{ij}^{*-1/2} \varphi_j^*(\mathbf{r})} h(\mathbf{r})\, \underbrace{\psi_i(\mathbf{r})}_{\sum_k S_{ik}^{-1/2} \varphi_k(\mathbf{r})}$$

$$= \sum_j S_{ji}^{-1/2} \varphi_j^*(\mathbf{r})$$

$$= \sum_{jk} \underbrace{\left(\sum_i S_{ji}^{-1/2} S_{ik}^{-1/2} \right)}_{S_{jk}^{-1}} \int d\mathbf{r}\, \varphi_j^*(\mathbf{r})\, \varphi_k(\mathbf{r})$$

$$\therefore\ E[\{\varphi_i(\mathbf{r})\}, v_H(\mathbf{r})] = \sum_{ij} \int d\mathbf{r}\, S_{ij}^{-1}\, \varphi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m^*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right] \varphi_j(\mathbf{r})$$
$$+ \frac{\epsilon}{8\pi e^2} \int d\mathbf{r}\, v_H(\mathbf{r})\, \nabla^2 v_H(\mathbf{r}) \qquad (33)$$

(Eular-Lagrange Equation w.r.t. $\varphi_i(\mathbf{r})$)

Now we can get the Eular-Lagrange equation without using Lagrange multipliers.

First, note that

$$\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} \sum_k S_{jk}^{-1} S_{kl} = \frac{\delta}{\delta\varphi_i^*(\mathbf{r})} \delta_{jl} = 0$$

$$\sum_k \left[\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} S_{jk}^{-1}\right] S_{kl} + \sum_k S_{jk}^{-1} \underbrace{\frac{\delta S_{kl}}{\delta\varphi_i^*(\mathbf{r})}}_{\frac{\delta}{\delta\varphi_i^*(\mathbf{r})}\int d\mathbf{r}'\varphi_l^*(\mathbf{r}')\varphi_k(\mathbf{r}) = \delta_{il}\varphi_k(\mathbf{r})} = 0$$

$$\sum_k \left[\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} S_{jk}^{-1}\right] S_{kl} + \delta_{il} \sum_k S_{jk}^{-1} \varphi_k(\mathbf{r}) = 0$$

$\sum_l S_{lm}^{-1} \times$ (above)

$$\underbrace{\sum_k \left[\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} S_{jk}^{-1}\right] \underbrace{\sum_l S_{kl} S_{lm}^{-1}}_{\delta_{km}}}_{\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} S_{jm}^{-1}} + \sum_k S_{jk}^{-1} \varphi_k(\mathbf{r}) S_{im}^{-1}$$

$$\boxed{\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} S_{jk}^{-1} = - S_{ik}^{-1} \sum_l S_{jl}^{-1} \varphi_l(\mathbf{r}) \qquad (34)}$$

Using Eq. (34),

$$\frac{\delta}{\delta\varphi_i^*(\mathbf{r})}E = \sum_j S_{ij}^{-1} h(\mathbf{r})\varphi_j(\mathbf{r}) + \sum_{jk} \frac{\delta S_{jk}^{-1}}{\delta\varphi_i^*(\mathbf{r})}\langle j|h|k\rangle$$

$$= \sum_j S_{ij}^{-1} h(\mathbf{r})\varphi_j(\mathbf{r}) - \sum_{jkl}\langle j|h|k\rangle S_{ik}^{-1} S_{jl}^{-1}\varphi_l(\mathbf{r}) \qquad (35)$$

At an orthonormal functional-space point,

$$\frac{\delta E}{\delta\varphi_i^*(\mathbf{r})} = h(\mathbf{r})\varphi_i(\mathbf{r}) - \underbrace{\sum_{jkl}\langle j|h|k\rangle \delta_{ik}\delta_{jl}\varphi_l(\mathbf{r})}_{\sum_j \langle j|h|i\rangle \varphi_j(\mathbf{r})}$$

$$\therefore R_i(\mathbf{r}) = -\frac{\delta E}{\delta\varphi_i^*(\mathbf{r})}$$

$$= -\left\{ h(\mathbf{r})\varphi_i(\mathbf{r}) - \sum_j \varphi_j(\mathbf{r})\langle j|h|i\rangle \right\} \qquad (36)$$

where

$$h(\mathbf{r}) = -\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \qquad (37)$$

If we perform a **subspace diagonalization** of $\langle j|h|i\rangle$, then

$$\boxed{R_i(\mathbf{r}) = -\left[\, h(\mathbf{r}) - \langle i|h|i\rangle \,\right] \varphi_i(\mathbf{r}) \qquad (38)}$$

8. Gradient w.r.t. $v_H(\mathbf{r})$

$$\boxed{\begin{aligned} G(\mathbf{r}) &\equiv -\frac{\partial E}{\partial v_H(\mathbf{r})} \\ &= -\left[\frac{\epsilon}{8\pi e^2} \nabla^2 v_H(\mathbf{r}) + n(\mathbf{r}) \right] \qquad (39) \end{aligned}}$$

§. Conjugate Gradient Method.

Start from $\{\psi_i^{(0)}(\mathbf{r}) \mid \text{orthonormal}\}$, $v_H^{(0)}(\mathbf{r})$

$$n^{(0)}(\mathbf{r}) = \sum_i |\psi_i^{(0)}(\mathbf{r})|^2, \quad h^{(0)}(\mathbf{r}) = -\frac{\hbar^2}{2m_*}\nabla^2 + v_{ext}(\mathbf{r}) + v_H^{(0)}(\mathbf{r}) + v_{xc}(\mathbf{r})$$

Subspace diagonalization, $\langle \psi_i^{(0)} | h^{(0)} | \psi_j^{(0)} \rangle$; get new $\{\psi_i^{(0)}(\mathbf{r})\}$ & $\varepsilon_i^{(0)}$

$$R_i^{(0)}(\mathbf{r}) = -\,[\,h^{(0)}(\mathbf{r}) - \varepsilon_i^{(0)}]\,\psi_i^{(0)}(\mathbf{r})$$

Gram-Schmidt orthogonalization, $R_i^{(0)}(\mathbf{r}) \leftarrow R_i^{(0)}(\mathbf{r}) - \sum_j \psi_i^{(0)}(\mathbf{r}) \langle \psi_j^{(0)} | R_i^{(0)} \rangle$

$$Y_i^{(0)}(\mathbf{r}) = R_i^{(0)}(\mathbf{r})$$

$$G^{(0)}(\mathbf{r}) = -\left[\frac{\epsilon}{8\pi e^2}\nabla^2 v_H^{(0)}(\mathbf{r}) + n^{(0)}(\mathbf{r})\right]$$

$$Z^{(0)}(\mathbf{r}) = G^{(0)}(\mathbf{r})$$

do $n = 0$, Ncgmax

Line minimize $E[\{\psi_i^{(n)}(\mathbf{r}) + \theta Y_i^{(n)}(\mathbf{r})\}, v_H^{(n)}(\mathbf{r}) + \theta Z^{(n)}(\mathbf{r})]$

if $(|E^{(n+1)} - E^{(n)}| < \epsilon)$ return

Subspace diagonalization of $\langle \psi_i^{(n+1)} | h^{(n+1)} | \psi_i^{(n+1)} \rangle$, get new $\{\psi_i^{(n+1)}(\mathbf{r})\}$ & $\varepsilon_i^{(n+1)}$

$$R_i^{(n+1)} = -\,[h^{(n+1)}(\mathbf{r}) - \varepsilon_i^{(n+1)}]\,\psi_i^{(n+1)}(\mathbf{r})$$

Orthogonalize $R_i^{(n+1)} \leftarrow R_i^{(n+1)} - \sum_j \psi_j^{(n+1)}(\mathbf{r}) \langle \psi_j^{(n+1)} | R_i^{(n+1)} \rangle$

$$Y_i^{(n+1)}(\mathbf{r}) \longleftarrow R_i^{(n+1)}(\mathbf{r}) + \frac{\langle R_i^{(n+1)} | R_i^{(n+1)} \rangle}{\langle R_i^{(n)} | R_i^{(n)} \rangle} Y_i^{(n)}(\mathbf{r})$$

$$G^{(n+1)}(\mathbf{r}) = -\left[\frac{\epsilon}{8\pi e^2}\nabla^2 v_H^{(n+1)}(\mathbf{r}) + n^{(n+1)}(\mathbf{r})\right]$$

$$Z^{(n+1)}(\mathbf{r}) \longleftarrow G^{(n+1)}(\mathbf{r}) + \frac{\langle G^{(n+1)} | G^{(n+1)} \rangle}{\langle G^{(n)} | G^{(n)} \rangle} Z^{(n)}(\mathbf{r})$$

enddo