# Conjugate-Gradient Electronic-State Solver

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## §. Problem

Minimize

$$E[\psi(\mathbf{r})] = \frac{\int d\mathbf{r}\, \psi^*(\mathbf{r}) \left[ -\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) \right] \psi(\mathbf{r})}{\int d\mathbf{r}\, |\psi(\mathbf{r})|^2} \tag{1}$$

with a constraint,

$$\int d\mathbf{r}\, |\psi(\mathbf{r})|^2 = 1 \tag{2}$$

## §. Gradient

$$R(\mathbf{r}) \equiv -\frac{\delta E}{\delta \psi^*(\mathbf{r})}$$

$$= -\frac{1}{\langle\psi|\psi\rangle}\left[ -\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) \right]\psi(\mathbf{r}) + \frac{\langle\psi|h|\psi\rangle}{|\langle\psi|\psi\rangle|^2}\psi(\mathbf{r})$$

For a normalized wave function,

$$R(\mathbf{r}) = -\frac{\delta E}{\delta \psi^*(\mathbf{r})} = -\left[ h(\mathbf{r}) - \langle\psi|h|\psi\rangle \right]\psi(\mathbf{r}) \tag{3}$$

where

$$h(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla + v(\mathbf{r}) \tag{4}$$

## §. Line Minimization

Let $\psi(\mathbf{r})$ & $\Upsilon(\mathbf{r})$ be a wave function & a search direction. Suppose $\langle\psi|\Upsilon\rangle = 0$.

$$\phi(\mathbf{r}) = \cos\theta\, \psi(\mathbf{r}) + \sin\theta\, \Upsilon(\mathbf{r}) \tag{5}$$

Then,

$$\begin{aligned} E(\theta) &= \langle \cos\theta\psi + \sin\theta\Upsilon | h | \cos\theta\psi + \sin\theta\Upsilon\rangle \\ &= \cos^2\theta \langle\psi|h|\psi\rangle + \sin\theta\cos\theta\,(\langle\psi|h|\Upsilon\rangle + \langle\Upsilon|h|\psi\rangle) \\ &\qquad + \sin^2\theta\, \langle\Upsilon|h|\Upsilon\rangle \end{aligned} \tag{6}$$

$$\begin{aligned} \frac{\partial E}{\partial\theta} &= -2\cos\theta\sin\theta\, h_{\psi\psi} + \cos2\theta\,(h_{\psi\Upsilon} + h_{\Upsilon\psi}) \\ &\qquad + 2\sin\theta\cos\theta\, h_{\Upsilon\Upsilon} \end{aligned}$$

$$\therefore \frac{\partial E}{\partial\theta} = 2\cos2\theta\, \mathrm{Re}\, h_{\Upsilon\psi} + \sin2\theta\,(h_{\psi\psi} + h_{\Upsilon\Upsilon}) \tag{7}$$

$$\therefore \frac{\partial^2 E}{\partial\theta^2} = -4\sin2\theta\, \mathrm{Re}\, h_{\Upsilon\psi} + 2\cos2\theta\,(h_{\psi\psi} + h_{\Upsilon\Upsilon}) \tag{8}$$

$$E\Big|_{\theta=0} = h_{\psi\psi} \tag{9}$$

$$\frac{\partial E}{\partial\theta}\Big|_{\theta=0} = 2\mathrm{Re}\, h_{\Upsilon\psi} \tag{10}$$

$$\frac{\partial^2 E}{\partial\theta^2}\Big|_{\theta=0} = 2(h_{\psi\psi} + h_{\Upsilon\Upsilon}) \tag{11}$$

(Line Minimization)

Let $\psi(\mathbf{r})$ & $Y(\mathbf{r})$ be a wave function & a search direction. Suppose $\langle\psi|Y\rangle = 0$ & $\langle\psi|\psi\rangle = \langle Y|Y\rangle = 1$. Line search which conserves the normalization is achieved by

$$\boxed{\psi_\theta(\mathbf{r}) = \cos\theta\,\psi(\mathbf{r}) + \sin\theta\,Y(\mathbf{r})} \qquad (5)$$

$$\because \langle\psi_\theta|\psi_\theta\rangle = \cos^2\theta\underbrace{\langle\psi|\psi\rangle}_{1} + \sin\theta\cos\theta(\cancel{\langle\psi|Y\rangle} + \cancel{\langle Y|\psi\rangle}) + \sin^2\theta\underbrace{\langle Y|Y\rangle}_{1}$$
$$= 1 \quad //$$

$$E(\theta) = \langle\cos\theta\,\psi + \sin\theta\,Y|h|\cos\theta\,\psi + \sin\theta\,Y\rangle$$

$$= \underbrace{\cos^2\theta}_{\frac{1+\cos2\theta}{2}}\langle\psi|h|\psi\rangle + \underbrace{\sin\theta\cos\theta}_{\frac{1}{2}\sin2\theta}\big(\underbrace{\langle\psi|h|Y\rangle + \langle Y|h|\psi\rangle}_{2\mathrm{Re}\langle Y|h|\psi\rangle}\big) + \underbrace{\sin^2\theta}_{\frac{1-\cos2\theta}{2}}\langle Y|h|Y\rangle$$

$$\boxed{E(\theta) = \frac{h_{\psi\psi}+h_{YY}}{2} + \frac{h_{\psi\psi}-h_{YY}}{2}\cos2\theta + \mathrm{Re}\,h_{Y\psi}\sin2\theta} \qquad (6)$$

$$\frac{\partial E}{\partial\theta} = -(h_{\psi\psi}-h_{YY})\sin2\theta + 2\,\mathrm{Re}\,h_{Y\psi}\cos2\theta \qquad (7)$$

$$\boxed{\frac{\partial E}{\partial\theta} = 0 \rightarrow \quad \theta_{min} = \frac{1}{2}\tan^{-1}\left(\frac{2\,\mathrm{Re}\,h_{Y\psi}}{h_{\psi\psi}-h_{YY}}\right)} \qquad (8)$$

## §. Algorithm

Start from a normalized $\psi_0(\mathbf{r}) \rightarrow$ psir & psii

$$R_0(\mathbf{r}) = -[h(\mathbf{r}) - \langle\psi_0|\underbrace{h|\psi_0}_{\text{hpsir \& hpsii}}\rangle]\,\psi_0(\mathbf{r})$$

$$Y_0(\mathbf{r}) \leftarrow R_0(\mathbf{r})$$

$Y_0(\mathbf{r}) \leftarrow Y_0(\mathbf{r}) - \psi_0(\mathbf{r})\langle\psi_0|Y_0\rangle$; normalize $Y_0(\mathbf{r})$

do $n = 0$, Ncgmax

calculate $h_{\psi\psi}^{(n)}$, $h_{Y\psi}^{(n)}$, $h_{YY}^{(n)}$

$$\theta_{min}^{(n)} = \frac{1}{2}\tan^{-1}\left(\frac{2\,\mathrm{Re}\,h_{Y\psi}^{(n)}}{h_{\psi\psi}^{(n)} - h_{YY}^{(n)}}\right)$$

$$\Delta E(\theta_{min}) = \frac{h_{\psi\psi}^{(n)} - h_{YY}^{(n)}}{2}(\cos 2\theta_{min} - 1) + \mathrm{Re}\,h_{Y\psi}\sin 2\theta_{min}$$

$$\psi_{n+1}(\mathbf{r}) = \psi_n(\mathbf{r})\cos\theta_{min} + Y_n(\mathbf{r})\sin\theta_{min}$$

if $(\Delta E(\theta_{min}) < \epsilon)$ return $\psi_{n+1}(\mathbf{r})$

$$R_{n+1}(\mathbf{r}) = -[h(\mathbf{r}) - \langle\psi_{n+1}|h|\psi_{n+1}\rangle]\,\psi_{n+1}(\mathbf{r})$$

$$Y_{n+1}(\mathbf{r}) \leftarrow R_{n+1}(\mathbf{r}) + \frac{\langle R_{n+1}|R_{n+1}\rangle}{\langle R_n|R_n\rangle}Y_n(\mathbf{r})$$

$Y_{n+1}(\mathbf{r}) \leftarrow Y_{n+1}(\mathbf{r}) - \psi_{n+1}(\mathbf{r})\langle\psi_{n+1}|Y_{n+1}\rangle$; normalize $Y_{n+1}(\mathbf{r})$

enddo