Functional Derivative Basics

- Let $f(\mathbb{r}) \in \mathbb{R}$ be a function of $\mathbb{r} \in \mathbb{R}^N$, and a functional $E[f(\mathbb{r})] \in \mathbb{R}$, whose value depends on $f(\mathbb{r})$.

- Let δE be the change in E due to the change $f(\mathbb{r}) \to f(\mathbb{r}) + \delta f(\mathbb{r})$. Then, the functional derivative $\delta E / \delta f(\mathbb{r})$ is defined through the relation,

$$\delta E = \int_{-\infty}^{\infty} d\mathbb{r} \frac{\delta E}{\delta f(\mathbb{r})} \delta f(\mathbb{r}) \qquad (1)$$

show examples 1 & 2 (PP.④-⑤)

- Complex function

  Let $\psi(\mathbb{r}) = \psi_1(\mathbb{r}) + i\psi_2(\mathbb{r})$ and $\psi^*(\mathbb{r}) = \psi_1(\mathbb{r}) - i\psi_2(\mathbb{r})$. Instead of regarding $\psi_1(\mathbb{r})$ & $\psi_2(\mathbb{r})$ as independent functions to be determined, we will regard $\psi(\mathbb{r})$ & $\psi^*(\mathbb{r})$ as independent functions.

- Rayleigh-Ritz variational principle

  Determine $\psi(\mathbb{r})$ to minimize the energy

$$E[\psi(\mathbb{r})] = \frac{\int d\mathbb{r}\, \psi^*(\mathbb{r}) \underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbb{r})\right]}_{h(\mathbb{r})} \psi(\mathbb{r})}{\int d\mathbb{r}\, \psi^*(\mathbb{r})\psi(\mathbb{r})} \qquad (2)$$

  At the minimum, the energy is stationary w.r.t. the change in $\psi(\mathbb{r})$ (or $\psi^*(\mathbb{r})$). Let $\psi^*(\mathbb{r}) \to \psi^*(\mathbb{r}) + \delta\psi^*(\mathbb{r})$.

$$E[\psi^*(\mathbb{r}) + \delta\psi^*(\mathbb{r})] = \frac{\int d\mathbb{r}\, (\psi^*(\mathbb{r}) + \delta\psi^*(\mathbb{r}))\, h(\mathbb{r})\, \psi(\mathbb{r})}{\int d\mathbb{r}\, (\psi^*(\mathbb{r}) + \delta\psi^*(\mathbb{r}))\, \psi(\mathbb{r})}$$

$$= \left(\langle\psi|h|\psi\rangle + \langle\delta\psi|h|\psi\rangle\right) \frac{1}{\langle\psi+\delta\psi|\psi\rangle}$$

$$\frac{1}{\langle\psi|\psi\rangle + \langle\delta\psi|\psi\rangle} = \frac{1}{\langle\psi|\psi\rangle} \frac{1}{1 + \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle}} = \frac{1}{\langle\psi|\psi\rangle}\left(1 - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + \cdots\right)$$

$$\therefore E[\psi^*(\mathbf{r})+\delta\psi^*(\mathbf{r})] = \frac{\langle\psi|h|\psi\rangle + \langle\delta\psi|h|\psi\rangle}{\langle\psi|\psi\rangle}\left(1 - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + \cdots\right)$$

$$= \underbrace{\frac{\langle\psi|h|\psi\rangle}{\langle\psi|\psi\rangle}}_{E[\psi^*(\mathbf{r})]} + \frac{\langle\delta\psi|h|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|h|\psi\rangle}{\langle\psi|\psi\rangle^2}\langle\delta\psi|\psi\rangle + \cdots$$

$$\therefore \delta E = \frac{1}{\langle\psi|\psi\rangle}\int d\mathbf{r}\, \delta\psi^*(\mathbf{r})\, h(\mathbf{r})\, \psi(\mathbf{r}) - \frac{\langle\psi|h|\psi\rangle}{\langle\psi|\psi\rangle^2}\int d\mathbf{r}\, \delta\psi^*(\mathbf{r})\, \psi(\mathbf{r}) \qquad (3)$$

Compare the defintion of the functional derivative, Eq. (1), with Eq. (3), we obtain

$$\frac{\delta E}{\delta\psi^*(\mathbf{r})} = \frac{1}{\langle\psi|\psi\rangle}\left[h(\mathbf{r})\psi(\mathbf{r}) - \frac{\langle\psi|h|\psi\rangle}{\langle\psi|\psi\rangle}\psi(\mathbf{r})\right] \qquad (4)$$

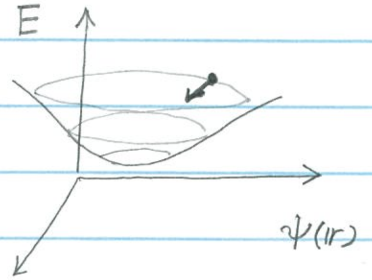
For a normalized wave function, $\langle\psi|\psi\rangle = 1$,

$$\frac{\delta E}{\delta\psi^*(\mathbf{r})} = \left(h(\mathbf{r}) - \langle\psi|h|\psi\rangle\right)\psi(\mathbf{r}) \qquad (5)$$

where

$$\begin{cases} h(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) & (6) \\ \langle\psi|h|\psi\rangle = \int d\mathbf{r}\, \psi^*(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r})\right]\psi(\mathbf{r}) & (7) \end{cases}$$

- Gradient-based minimization



$$\psi(\mathbf{r}) \leftarrow \psi(\mathbf{r}) - \delta\tau \underbrace{\left(h(\mathbf{r}) - \langle \psi | h | \psi \rangle \right)}_{\text{residual.}} \psi(\mathbf{r})$$

as long as it's nonzero

- Better approach = conjugate gradient
  [Show Payne RMP '92]
  or
  Molecular dynamics = fictitious dynamics using the gradient as force
  [Show Car-Parrinello '85]

- Example 1

$$E[f(\mathbb{r})] = \int d\mathbb{r}\, f(\mathbb{r})^2$$

$$E[f(\mathbb{r})+\delta f(\mathbb{r})] - E[f(\mathbb{r})]$$

$$= \int d\mathbb{r} \left\{ \underbrace{[f(\mathbb{r}) + \delta f(\mathbb{r})]^2 - f^2(\mathbb{r})}_{\cancel{f^2(\mathbb{r})} + 2f(\mathbb{r})\delta f(\mathbb{r}) + \cancel{\delta f^2(\mathbb{r})} - \cancel{f^2(\mathbb{r})}} \right\}$$

$$= \int d\mathbb{r}\; 2f(\mathbb{r})\,\delta f(\mathbb{r})$$

$$\therefore \frac{\delta E}{\delta f(\mathbb{r})} = 2f(\mathbb{r})$$

- Example 2

$$E[\rho(\mathbf{r})] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E[\rho(\mathbf{r})+\delta\rho(\mathbf{r})] - E[\rho(\mathbf{r})]$$

$$= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \frac{[\rho(\mathbf{r})+\delta\rho(\mathbf{r})][\rho(\mathbf{r}')+\delta\rho(\mathbf{r}')] - \rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \frac{\overset{\mathbf{r}\leftrightarrow\mathbf{r}'}{\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')} + \delta\rho(\mathbf{r})\,\rho(\mathbf{r}') + \cancel{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \int d\mathbf{r}\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\delta\rho(\mathbf{r})$$

$$\therefore \frac{\delta E[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$