FYS4411/9411 FEB 18

$$\mathbb{E}[E_L(\vec{\alpha})] = \int d\vec{R}\, P(\vec{R},\vec{\alpha}) E_L(\vec{R},\vec{\alpha})$$

$$(\langle E_L(\vec{\alpha})\rangle)$$

$$P(\vec{R},\vec{\alpha}) = \frac{|\psi_T(\vec{R},\vec{\alpha})|^2}{\int d\vec{R}\, |\psi_T(\vec{R},\vec{\alpha})|^2}$$

$$E_L(\vec{R},\vec{\alpha}) = \frac{1}{\psi_T(\vec{R},\vec{\alpha})} H(\vec{R})\psi_T(\vec{R},\vec{\alpha})$$

$$\psi_T(\vec{R},\vec{\alpha}) \longrightarrow \psi(\vec{\alpha})$$

$$\frac{\partial\, \mathbb{E}[E_L(\vec{\alpha})]}{\partial\vec{\alpha}} = 0$$

$$= \int d\vec{R}\left[\frac{dp(\vec{\alpha})}{d\alpha} E_L(\vec{\alpha}) + p(\vec{\alpha})\frac{dE_L(\vec{\alpha})}{d\alpha}\right]$$

Example: $\psi(\vec{\alpha}) = \psi(\alpha)$

$$= e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\frac{dp(\alpha)}{d\alpha} = \frac{d}{d\alpha}\frac{|e^{-\frac{1}{2}\alpha^2x^2}|^2}{\int dx\, e^{-\alpha^2x^2}}$$

$$d\alpha \qquad d\alpha \int dx\, e$$

$$= \frac{-2\alpha x^2 e^{-\alpha^2 x^2} \int dx\, e^{-\alpha^2 x^2} + \left[\int 2\alpha x^2 e^{-\alpha^2 x^2}\right] \cdot e^{-\alpha^2 x^2}}{\left(\int dx\, e^{-\alpha^2 x^2}\right)^2}$$

$$= -\frac{2\alpha x^2 e^{-\alpha^2 x^2}}{\int e^{-\alpha^2 x^2} dx} + \frac{e^{-\alpha^2 x^2}}{\int e^{-\alpha^2 x^2} dx} \frac{\int 2\alpha x^2 e^{-\alpha^2 x^2} dx}{\int e^{-\alpha^2 x^2} dx}$$

$$P(\alpha) \qquad \boxed{P(\alpha)}\boxed{\int 2\alpha x^2 P(\alpha)\, dx}$$

$$-2\alpha x^2 \frac{e^{-\alpha^2 x^2 \cdot 1/2}}{e^{-\alpha^2 x^2 \cdot 1/2}} = 2\, \frac{\frac{d\psi(\alpha)}{d\alpha}}{\psi(\alpha)}$$

$$= 2 \frac{d}{d\alpha} \ln \psi(\alpha)$$

$$-2 \int P(\alpha) \frac{d}{d\alpha} \ln \psi(\alpha)\, dx$$

$$\int dx \frac{dP(\alpha)}{d\alpha} E_2(\alpha)$$

$$= 2\left[\overline{\int dx \left\{\frac{d\ln\psi(\alpha)}{d\alpha} E_L(\alpha)\right.}\right.$$

$$\left.\left. - \underline{P(\alpha) E_L(\alpha)} \int \underline{\frac{d\ln\psi(\alpha)}{d\alpha} P(\alpha)} \right\}\right]$$

$$= 2\left[\mathbb{E}\left[\frac{d\ln\psi(\alpha)}{d\alpha} E_L(\alpha)\right] - \mathbb{E}\left[\frac{d\ln\psi(\alpha)}{d\alpha}\right]\mathbb{E}\left[E_L(\alpha)\right]\right] = 0$$

new integral, new integral

multi-dim evaluate by MC integration

$$\frac{d\,\mathbb{E}[E_L(\alpha)]}{d\alpha}$$

in general $\vec{\nabla}_{\vec{\alpha}} \mathbb{E}[E_L(\vec{\alpha})]$

steepest descent

$$\vec{\alpha}^{\,opt} = \underset{\vec{\alpha} \in \mathbb{R}^M}{\arg\min}\ \mathbb{E}[E_L(\vec{\alpha})]$$

solve iteratively

$$\vec{\alpha}^{(k+1)} = \vec{\alpha}^{(k)} - \gamma \vec{\nabla}_{\vec{\alpha}} \mathbb{E}\left[E_L(\vec{\alpha})\right]_{\vec{\alpha}^{(k)}}$$

γ ↗ learning rate

stop when

$$\|\vec{\alpha}^{(k+1)} - \alpha^{(k)}\|_2 \le \delta \approx 10^{-8}$$

Example : 2 electrons in two-dim interact via an electrostatic potential

$$\psi_T(\vec{R}, \alpha, \beta) = e^{-\frac{\alpha^2}{2}(r_1^2 + r_2^2)} \times J(r_{12})$$

$$\vec{R} = \{\vec{r}_1, \vec{r}_2\}$$

$$r_i = \sqrt{x_i^2 + y_i^2}$$

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$$

$$J(r_{12}) = e^{\frac{r_{12}}{1 + \beta r_{12}}}$$

- code ;

(+) importance sampling

(+) analytical E_L

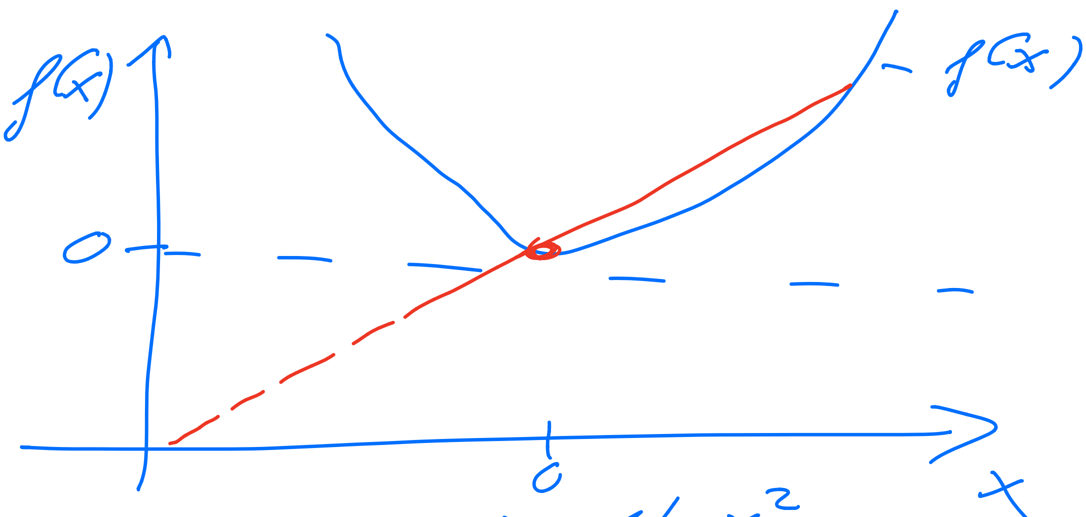
(+) — " — quantum force

$\Rightarrow$ + numerical $\vec{\nabla}_{\alpha,\beta} \mathbb{E}[E_L(\alpha,\beta)]$

— Gradient algos —

$$\mathbb{E}[E_L(\vec{\alpha})] \longrightarrow f(\vec{x})$$

$$\vec{\nabla}_{\vec{x}} f(\vec{x}) = \vec{\nabla} f(\vec{x}) = 0$$



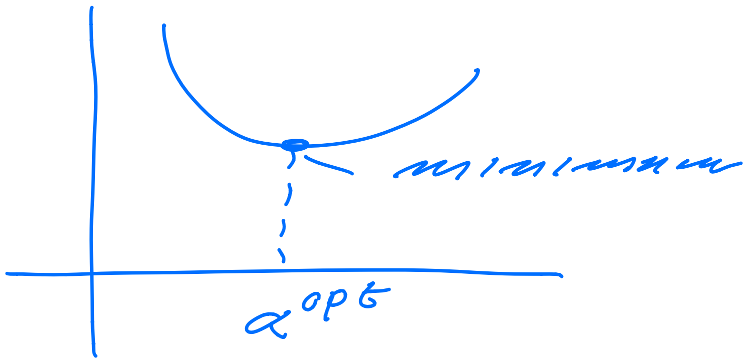
$$f(x) = 1/2\, x^2$$
$$f'(x) = x$$

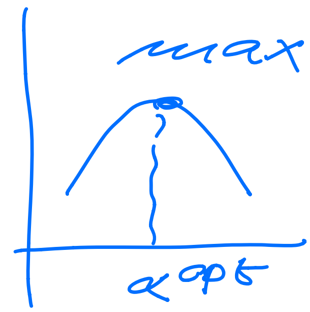
$f'(x) = 0$, min.

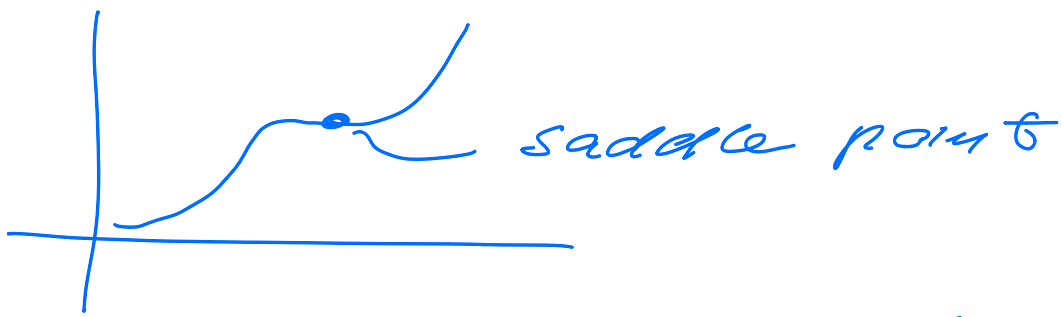
$x < 0$
$f'(x) < 0$
$f(x)$ is decreased
by moving to

$x > 0$
$f'(x) > 0$
move to
the left.

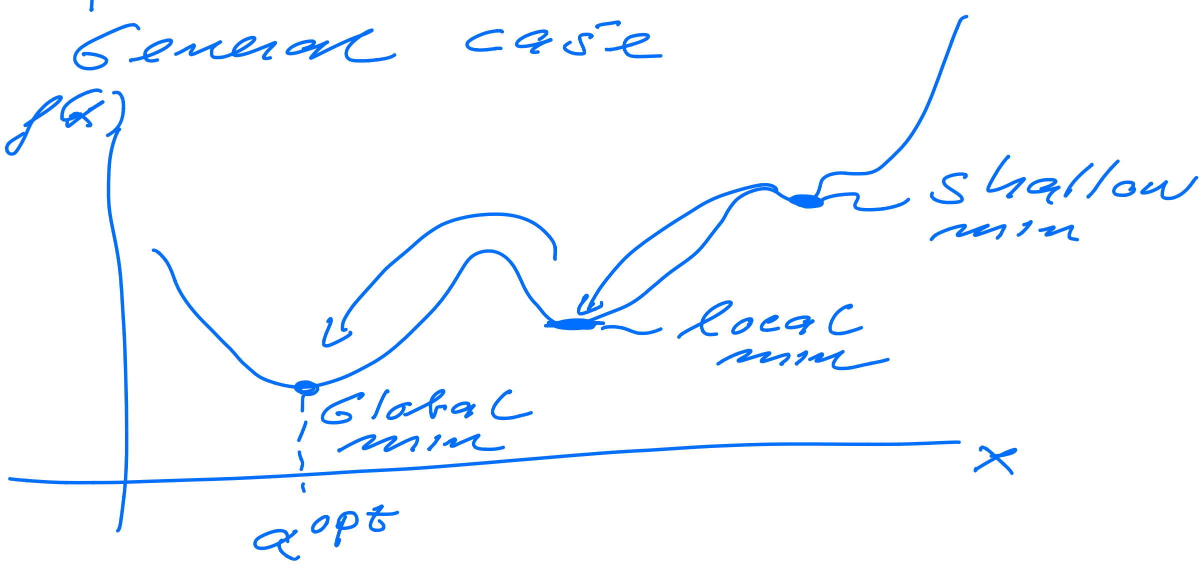
the right







General case



2nd derivative:

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = H_{ij} = \text{Hessian matrix}$$

$$= H_{ji}$$

In most cases H is positive definite, all eigenvalues are larger than zero

$\Rightarrow$ convex optimization

Taylor-expansion of $f(\vec{x})$ around $\vec{x}_0$

$$f(\vec{x}) \cong f(\vec{x}_0) + \underbrace{(\vec{x}-\vec{x}_0)^T}_{\gamma\vec{g}^T}\vec{g}$$

$$(\vec{g} = \vec{\nabla} f(\vec{x}))$$

$$+ \frac{1}{2}(\vec{x}-\vec{x}_0)^T H(\vec{x}-\vec{x}_0)$$

use a learning rate γ

new point:

$$\vec{x} \cong \vec{x}_0 - \underline{\gamma \cdot \vec{g}}$$

$$f(\vec{x}) = f(\vec{x}_0 - \gamma\vec{g}) \cong f(\vec{x}_0)$$

$$- \gamma\vec{g}^T\vec{g} + \frac{1}{2}\gamma^2\vec{g}^T H\vec{g}$$

optimal γ $\quad \frac{df(\vec{x})}{d\gamma} =$

$$\vec{g}^T\vec{g} = \gamma\vec{g}^T H\vec{g} \Rightarrow$$

$$\underline{\gamma}^{opt} = \frac{\vec{g}^T \vec{g}}{\vec{g}^T \underline{\underline{H}}\, \vec{g}}$$

Newton-Raphson

$$\vec{x}^{(k+1)} = \vec{x}^{(k)} - \underline{\left[H(f(\vec{x}^{(k)})) \right]^{-1}} \times \vec{\nabla} f(\vec{x}^{(k)})$$