Variacijska metoda

$$I_{(y)} = \int f(x, y, y', \dots)\, dx$$

$$I(y_0) = \text{MIN}$$

$$I(y) > I(y_0)$$

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\langle \psi | \psi \rangle = 1$$

$$\Downarrow$$

$$E = \langle \psi | \hat{H} | \psi \rangle = \int \psi^* \hat{H} \psi \, dV$$

$$\Downarrow$$

$$\underline{H\psi = E\psi}$$

Če mi ne moremo rešiti prave Schrödingerjeve enačbe, si zamislimo PRIBLIŽNO FUNKCIJO!

$$\boxed{\psi = \sum_i c_i \psi_i}$$

osnovno stanje v nesk. pot. jami

$$\psi = \sqrt{\frac{1}{a}} \cos \frac{\pi x}{2a}$$

$$\psi = N(x-a)(x+a)$$

$\langle \psi | \psi \rangle = 1$; normirana funkcija $\Rightarrow$

$$\boxed{\sum_i |c_i|^2 = 1}$$

$$\underline{\hat{H}\psi} = \hat{H} \sum_i c_i \psi_i = \sum_i c_i \hat{H} \psi_i = \underline{\sum_i c_i E_i \psi_i}$$

$$E_0 < E_1 < E_2 < \dots$$

$$\underline{E = \langle \psi | \hat{H} \psi \rangle} = \sum_i \underline{|c_i|^2 E_i} \geq \sum_i |c_i|^2 E_0$$

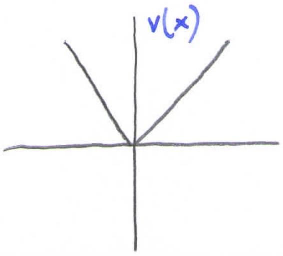
$$\boxed{E > E_0}$$

$$\psi = f(a, b, c \dots)$$

$E = \langle \psi | \hat{H} | \psi \rangle = g(a, b, c \dots)$ ~ najmanjšo vrednost ima funkcija v minimumu →

→ ko je gradient $= 0$ $\Rightarrow$ $\frac{\partial E}{\partial a} = 0$, $\frac{\partial E}{\partial b} = 0$, $\frac{\partial E}{\partial c} = 0 \dots$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \beta|x|$$



$$\hat{H}\psi = E\psi$$

Airjeve funkcije :

$$E_0 = 1{,}49212\sqrt[3]{\frac{\hbar^2\beta^2}{2\pi m}}$$

$\downarrow$ poenostavimo oz. izračunamo približek

$$\boxed{\psi = N\cdot e^{-\frac{\lambda x^2}{4}}}$$

~ ne sme imeti ničle

~ $x \to \infty$, $\to -\infty$ gre vrednost proti 0

Normiramo :

$$\langle\psi|\psi\rangle = 1$$

$$\int_{-\infty}^{\infty} N^2 e^{-\frac{\lambda x^2}{2}}dx = N^2\int_{-\infty}^{\infty} e^{-\frac{\lambda x^2}{2}}dx = 2N^2\int_0^{\infty} e^{-\frac{\lambda x^2}{2}}dx = \cancel{2}N^2\frac{\sqrt{\pi}\sqrt{2}}{\cancel{2}\sqrt{\lambda}} = 1$$

Bronštejn : $\int_0^{\infty} e^{-a^2x^2}dx = \frac{\sqrt{\pi}}{2a}$

$$\Downarrow$$

$$N = \sqrt[4]{\frac{\lambda}{2\pi}}$$

$$\psi = \sqrt[4]{\frac{\lambda}{2\pi}}\, e^{-\frac{\lambda x^2}{4}}$$

$$E = \langle\psi|\hat{H}|\psi\rangle = \int_{-\infty}^{\infty}\psi^*\hat{H}\psi\, dx = \int_{-\infty}^{\infty}\sqrt[4]{\frac{\lambda}{2\pi}}e^{-\frac{\lambda x^2}{4}}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\beta|x|\right)\sqrt[4]{\frac{\lambda}{2\pi}}e^{-\frac{\lambda x^2}{4}}dx =$$

$$= \sqrt[2]{\frac{\lambda}{2\pi}}\int_{-\infty}^{\infty}\left(e^{-\frac{\lambda x^2}{4}}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{-\frac{\lambda x^2}{4}}\right) + e^{-\frac{\lambda x^2}{4}}\left(\beta|x|e^{-\frac{\lambda x^2}{4}}\right)\right)dx =$$

$$= \sqrt[2]{\frac{\lambda}{2\pi}}\int_{-\infty}^{\infty}\left[-\frac{\hbar^2}{2m}\left(e^{-\frac{\lambda x^2}{2}}\frac{\lambda^2x^2}{4} - e^{-\frac{\lambda x^2}{2}}\frac{\lambda}{2}\right) + \beta|x|e^{-\frac{\lambda x^2}{2}}\right)dx =$$

$$\left(e^{-\frac{\lambda x^2}{4}}\right)'' = \left(e^{-\frac{\lambda x^2}{4}}\cdot\left(\frac{-\lambda x}{2}\right)\right)' = \underline{e^{-\frac{\lambda x^2}{4}}\frac{\lambda x^2}{4} - \frac{\lambda}{2}e^{-\frac{\lambda x^2}{4}}}$$

naslednja stran

iz Bronštejna:

$$\int_0^\infty x e^{-a^2x^2}dx = \frac{1}{2a^2}$$

$$\int_0^\infty x^2 e^{-a^2x^2}dx = \frac{\sqrt{\pi}}{4a^3}$$

$$= 2\sqrt{\frac{\lambda}{2\pi}}\left[-\frac{\hbar^2}{2m}\left(\frac{\lambda^2}{2m}\left(\frac{\lambda^2}{4}\frac{\sqrt{\pi}(\sqrt{2})^3}{4(\sqrt{\lambda})^3}-\frac{\lambda}{2}\frac{\sqrt{\pi}\sqrt{2}}{2\sqrt{\lambda}}\right)+\beta\frac{1(\sqrt{2})^2}{2(\sqrt{\lambda})^2}\right]=$$

$$= 2\frac{\sqrt{\lambda}}{2\pi}\left[\frac{-\hbar^2}{2m}\left(\underbrace{\frac{\cancel{\lambda}\lambda^{\cancel{2}}}{4}\frac{\sqrt{\pi}\sqrt{2}\cancel{2}}{2\cancel{4}\sqrt{\lambda}\cancel{\lambda}}}_{\frac{\sqrt{\lambda}\sqrt{\pi}\sqrt{2}}{8}}-\underbrace{\frac{\lambda\sqrt{\pi}\sqrt{2}}{4\sqrt{\lambda}}}_{\frac{\sqrt{\lambda}\sqrt{\pi}\sqrt{2}}{4}}\right)+\beta\frac{\cancel{2}}{\cancel{2}\lambda}\right]=$$

$$= \underbrace{\frac{\sqrt{\lambda}\sqrt{\pi}\sqrt{2}}{8}-\frac{\sqrt{\lambda}\sqrt{\pi}\sqrt{2}}{4}}_{-\frac{\sqrt{\lambda}\sqrt{\pi}\sqrt{2}}{8}} =$$

$$E = 2\sqrt{\frac{\lambda}{2\pi}}\left[-\frac{\hbar^2}{2m}\left(\frac{-\sqrt{\lambda\pi 2}}{8}\right)+\beta\frac{1}{\lambda}\right]=$$

$$E = \frac{\hbar^2}{2m}\frac{\lambda}{4}+\frac{2\beta\cancel{\sqrt{\lambda}}}{2\pi\cancel{\lambda}\sqrt{\lambda}} = \frac{\hbar^2}{8m}\lambda+\frac{2\beta}{\sqrt{2\pi}\sqrt{\lambda}}$$

$$\frac{\partial E}{\partial\lambda} = \frac{\hbar^2}{8m}-\frac{2\beta}{\sqrt{2\pi}}\frac{1}{2}\lambda^{-\frac{3}{2}}=0$$

$$\frac{\hbar^2}{8m}-\frac{\beta}{\sqrt{2\pi}\lambda^{\frac{3}{2}}}=0$$

$$\frac{\hbar^2}{8m}=\frac{\beta}{\sqrt{2\pi}\lambda^{\frac{3}{2}}}$$

$$\lambda^{\frac{3}{2}}=\frac{\beta 8m}{\hbar^2\sqrt{2\pi}} \Rightarrow \boxed{\lambda = \sqrt[3]{\left(\frac{8m\beta}{\hbar^2\sqrt{2\pi}}\right)^2}}$$

vstavimo v

$$\Downarrow$$

$$E = 1{,}5\sqrt[3]{\frac{\hbar^2\beta^2}{2\pi m}}$$

iz prejšnje strani:

$$E_0 = 1{,}49212\sqrt[3]{\frac{\hbar^2\beta^2}{2\pi m}}$$

$$\boxed{E \sim E_0}$$

$$\Psi = \sum_i \phi_i$$

izbrane funkcije

za nesk. pot. jamo

$$\phi_1 = (x-a)(x+a)$$

$$\phi_2 = (x-a)^2(x+a)^2$$

$\vdots$

$$\Psi = c_1\phi_1 + c_2\phi_2$$

$$\boxed{c_1, c_2 \in \mathbb{R}}$$

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle c_1\phi_1 + c_2\phi_2 | \hat{H} | c_1\phi_1 + c_2\phi_2 \rangle}{\langle c_1\phi_1 + c_2\phi_2 | c_1\phi_1 + c_2\phi_2 \rangle} =$$

$$= \frac{c_1^2 \langle \phi_1 | \hat{H} | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \hat{H} | \phi_2 \rangle + c_1 c_2 \langle \phi_2 | \hat{H} | \phi_1 \rangle + c_2^2 \langle \phi_2 | \hat{H} | \phi_2 \rangle}{c_1^2 \langle \phi_1 | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \phi_2 \rangle + c_1 c_2 \langle \phi_2 | \phi_1 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle} =$$

$H_{11} = \langle \phi_1 | \hat{H} | \phi_1 \rangle$

$H_{12} = \langle \phi_1 | \hat{H} | \phi_2 \rangle = H_{21}$

$H_{22} = \langle \phi_2 | \hat{H} | \phi_2 \rangle$

$S_{11} = \langle \phi_1 | \phi_1 \rangle$

$S_{22} = \langle \phi_2 | \phi_2 \rangle$

$S_{12} = S_{21} = \langle \phi_1 | \phi_2 \rangle = \langle \phi_2 | \phi_1 \rangle$

$$E = \frac{c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$\boxed{\frac{\partial E}{\partial c_1} = 0 \,, \quad \frac{\partial E}{\partial c_2} = 0}$$

da dobimo MIN

$$E(c_1^2 S_{11} + 2c_1c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1c_2 H_{12} + c_2^2 H_{22}$$

odvajamo po c_1 oz. $\frac{\partial}{\partial c_1}$

$$\cancel{\frac{\partial E}{\partial c_1}(\quad)} + E(\cancel{2}c_1 S_{11} + \cancel{2}c_2 S_{12}) = \cancel{2}c_1 H_{11} + \cancel{2}c_2 H_{12}$$

odvajamo po c_2 oz. $\frac{\partial}{\partial c_2}$

$$\cancel{\frac{\partial E}{\partial c_2}(\quad)} + E(\cancel{2}c_1 S_{12} + \cancel{2}c_2 S_{22}) = \cancel{2}c_1 H_{12} + \cancel{2}c_2 H_{22}$$

$$\boxed{\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned}}$$

zapišemo matriko

$$\begin{bmatrix} H_{11}-ES_{11}, & H_{12}-ES_{12} \\ H_{21}-ES_{12}, & H_{22}-ES_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

1) $\left.\begin{matrix} c_1=0 \\ c_2=0 \end{matrix}\right\}$ ni fizikalno

Izračunamo determinanto !

2)
$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{12} & H_{22}-ES_{22} \end{vmatrix} = 0 \qquad H_{21}=H_{12} \text{ !!}$$

$$(H_{11}-ES_{11})(H_{22}-ES_{22}) - (H_{12}-ES_{12})^2 = 0$$

Dobimo E_1, E_2 - gledamo najnižjo E

vstavimo v enačbo =>
lahko izračunamo c_1 in c_2 =>
lahko izračunamo energijo

SPLOŠNO :

$\phi_1 \dots \phi_n$

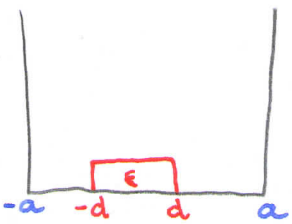
$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$$
$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

DETERMINANTA (matrika)

$$\begin{vmatrix} H_{11}-ES_{11} & \dots & H_{1n}-ES_{1n} \\ \vdots & \ddots & \vdots \\ H_{n1}-ES_{n1} & \dots & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

Perturbacijska metoda

$$\boxed{\hat{H} = \underbrace{\hat{H}_0}_{\text{znamo rešiti}} + \hat{H}'}$$ nas „zmoti"



$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V$$

$$V = V_0 + V'$$

$$V_0 = \begin{cases} \infty, & (x>a) \wedge (x<-a) \\ 0, & -a<x<a \end{cases}$$

$$V' = \begin{cases} 0, & (x>d) \wedge (x<-d) \\ \varepsilon, & -d<x<d \end{cases}$$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0}_{H_0} + V' \qquad \boxed{H' = V'}$$

$$E_n = \underbrace{E_n^0 + E_n^1\lambda + E_n^2\lambda^2 + E_n^3\lambda^3 + \dots}_{\text{Taylorjev razvoj}}$$

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$\lambda = 0 \sim$ kar znamo izračunati

$\lambda = 1 \sim$ popravki

$$\psi_n = \psi_n^0 + \psi_n^1\lambda + \psi_n^2\lambda^2 + \dots$$

$$\boxed{\hat{H}\psi_n = E_n\psi_n}$$

$$(\hat{H}_0 + \lambda H')(\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots) = (E_n^0 + E_n^1\lambda + E_n^2\lambda^2 + \dots)(\psi_n^0 + \psi_n^1\lambda + \dots)$$

$\boxed{\lambda^0}$ $\hat{H}_0\psi_n^0 = E_n^0\psi_n^0 \sim$ sistem, ki nima motenj : E_n^0, ψ_n^0

$\boxed{\lambda^1}$ $\hat{H}_0\underline{\psi_n^1} + H'\psi_n^0 = E_n^0\underline{\psi_n^1} + \underline{E_n^1}\psi_n^0$; ne poznamo ψ_n^1 in E_n^1

popravki funkcije 1. reda

Vzamemo bazo (E_n^0, ψ_n^0): $$\boxed{\psi_n^1 = \sum_i c_{in}\psi_i^0}$$

$$\underline{\hat{H}_0 \sum_i c_{in} \psi_i^0} + H^1 \psi_n^0 = E_n^0 \sum_i c_{in} \psi_i^0 + E_n^1 \psi_n^0$$

$$\sum_i c_{in} \hat{H}_0 \psi_i^0 = \sum_i c_{in} E_i^0 \psi_i^0$$

$$\sum_i c_{in} E_i^0 \psi_i^0 + H^1 \psi_n^0 = E_n^0 \sum_i c_{in} \psi_i^0 + E_n^1 \psi_n^0 \; / \cdot \psi_k^{0*}$$

$$\int \left(\sum_i c_{in} E_i^0 \psi_k^{0*} \psi_i^0 + \psi_k^{0*} H^1 \psi_n^0 \right) dV = \int \left(E_n^0 \sum_i c_{in} \psi_k^{0*} \psi_i^0 + E_n^1 \underbrace{\psi_k^{0*} \psi_n^0}_{1 \; \boxed{k=n}} \right) dV$$

① ko je $\boxed{k=n}$

$$\cancel{c_{nn} E_n^0} + \int \left(\psi_n^{0*} \hat{H}^1 \psi_n^0 \right) dV = \cancel{E_n^0 c_{nn}} + E_n^1$$

Popravek energije 1. reda:

$$E_n^1 = \langle \psi_n^0 | \hat{H}^1 | \psi_n^0 \rangle$$

② ko je $\boxed{k \neq n}$

$$c_{kn} E_k^0 + \int \psi_k^{0*} \hat{H}^1 \psi_n^0 \, dV = E_n^0 c_{kn}$$

$$c_{kn} (E_n^0 - E_k^0) = \langle \psi_k^{0*} | \hat{H}^1 | \psi_n^0 \rangle$$

$$\boxed{c_{kn} = \frac{\langle \psi_k^{0*} | \hat{H}^1 | \psi_n^0 \rangle}{E_n^0 - E_k^0}} \Rightarrow \psi_n^1 = \sum_{n \neq k} c_{kn} \psi_k^0$$

Popravek val. funkcije 1. reda:

Popravek E 2. reda:

$$E_n^2 = \sum_{n \neq k} \frac{|\langle \psi_n^0 | \hat{H}^1 | \psi_k^0 \rangle|^2}{E_n^0 - E_k^0}$$

$$\psi_n^2 = \sum_{m \neq n} \left\{ \left[\sum_{j \neq n} \frac{\langle \psi_j^0 | \hat{H}^1 | \psi_n^0 \rangle \langle \psi_m^0 | \hat{H}^1 | \psi_j^0 \rangle}{(E_n^0 - E_j^0)(E_n^0 - E_k^0)} - \frac{\langle \psi_n^0 | \hat{H}^1 | \psi_n^0 \rangle \langle \psi_m^0 | \hat{H}^1 | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2} \right] \psi_m^0 - \frac{|\langle \psi_m^0 | \hat{H}^1 | \psi_n^0 \rangle}{2(E_n^0 - E_m^0)^2} \psi_n^0 \right\}$$

He atom - perturbacijska teorija

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{z}{4\pi\varepsilon_0 r_1} - \frac{z}{4\pi\varepsilon_0 r_2}$$ } znamo rešiti - golo jedro

$$H^1 = \frac{-e_0^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$$ } motnja - odboj elektronov

helij:

$$\boxed{\begin{gathered}\hat{H}_0\Psi(1,2) = E_0\Psi(1,2)\\ \Psi_0^0(1,2) = 1s(1)\,1s(2)\end{gathered}}$$

$$E_0^1 = \langle\Psi_0^0|H^1|\Psi_0^0\rangle$$

znamo izračunati:

$$E_0^0 = 2E_1\,;\quad E_1 = \frac{-13{,}6\,\text{eV}\,z^2}{1^2} = -13{,}6\,\text{eV}\,z^2$$

$$E_0^1 = \frac{5z}{8}\cdot(27{,}2)\,\text{eV}$$

$z=2$:

$$E_0^0 = -108{,}8\text{ eV}$$

$$E_0^1 = 34\text{ eV}$$

$$E_0 = E_0^0 + E_0^1 = -74{,}8\text{ eV}$$

$$He \rightarrow e^- + He^+$$

$-74{,}8$ eV 0 $-54{,}4$ eV

$E_{i_1} = 20{,}4$ eV

1. ion. energija

$$He^+ \rightarrow e^- + He^{2+}$$

$-54{,}4$ eV 0 0 - jedro

$E_{i_2} = 54{,}4$ eV

2. ion. energija

Ti dve energiji sta po vrednostih zelo blizu eksperimentalnim opažanjem.

He atom - variacijska metoda

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{Ze_0^2}{4\pi\varepsilon_0 r_1} - \frac{Ze_0^2}{4\pi\varepsilon_0 r_2} + \frac{e_0^2}{4\pi\varepsilon_0 |\vec{r}_1-\vec{r}_2|}$$

$$1s = R_{10} Y_{00} = \left(\frac{z^3}{\pi}\right)^{\frac{1}{2}} \cdot e^{-zr}$$

$r \to \infty \Rightarrow z$ efektivni $= 1$

$r \to 0 \Rightarrow z$ efektivni $= 2$

$$1s(1) = \left(\frac{z_{ef}^3}{\pi}\right)^{\frac{1}{2}} \cdot e^{-z_{ef} r_1}$$

$$1s(2) = \left(\frac{z_{ef}^3}{\pi}\right)^{\frac{1}{2}} \cdot e^{-z_{ef} r_2}$$

$$E = \langle \Psi(1,2) | \hat{H} | \Psi(1,2) \rangle$$

$z = 2$

$$E = z_{ef}^2 - \frac{27}{8} z_{ef} \quad (\text{v atm.})$$

$\Downarrow$

$$\frac{\partial E}{\partial z_{ef}} = 0$$

$$2z_{ef} - \frac{27}{8} = 0$$

$$z_{ef} = \frac{27}{16} \quad (\text{v atm.})$$

med 1 in 2

(v atm.)

$$E = \left(\frac{27}{16}\right)^2 - \frac{27}{8} \cdot \frac{27}{16} =$$

$= -77{,}4563\ \text{eV}$ (v eV)

zelo blizu eks. določitvi $\Rightarrow$ zelo NATANČNEJŠA ENERGIJA