Ritzův variační princip

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \longrightarrow E_n = \frac{\langle\phi_n|\hat{H}|\phi_n\rangle}{\langle\phi_n|\phi_n\rangle}$$

Pro libovolnou funkci $|\Psi\rangle$ platí

$$E_{\text{odh}} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0$$

energie základního stavu

Dokažme RVP

$$1 = \sum_n |n\rangle\langle n|$$

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$E_{\text{odh}} - E_0 = \frac{\langle\Psi|\hat{H} - E_0|\Psi\rangle}{\langle\Psi|\Psi\rangle} =$$

$$= \sum_n \frac{\langle\Psi|\hat{H}|n\rangle\langle n|\Psi\rangle - E_0\langle\Psi|n\rangle\langle n|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

E_n

$$= \sum_n \frac{\overbrace{(E_n - E_0)}^{\geq 0}\,\overbrace{|\langle\Psi|n\rangle|^2}^{\geq 0}}{\underbrace{\langle\Psi|\Psi\rangle}_{>0\,=1}} \geq 0$$

Př:

$$H = \begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix} \rightarrow \text{základní stav lineárním variačním principem}$$

$$|\Psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \quad E_{\text{var}} = \langle\Psi|\hat{H}|\Psi\rangle = \left(a \;\; \sqrt{1-a^2}\right)\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix}\begin{pmatrix} a \\ \sqrt{1-a^2} \end{pmatrix}$$

$$= \underline{a\ \sqrt{\dots}} \begin{pmatrix} \varepsilon a + J\sqrt{1-a^2} \\ Ja + \varepsilon\sqrt{1-a^2} \end{pmatrix} = \varepsilon a^2 + Ja\sqrt{1-a^2} + Ja\sqrt{1-a^2} + \varepsilon(1-a^2)$$

$$= \varepsilon + 2Ja\sqrt{1-a^2}$$

$$\frac{\partial}{\partial a} E_{var} = 0 \Rightarrow \cancel{2}J\sqrt{1-a^2} + \cancel{2}Ja\frac{1}{\cancel{2}}\frac{-2a}{\sqrt{1-a^2}} = 0 \quad / \cdot \sqrt{1-a^2}$$

$$J(1-a^2) - Ja^2 = 0$$

$$J - 2Ja^2 = 0 \Rightarrow a^2 = \frac{1}{2}$$

$$\boxed{a = \pm\frac{1}{\sqrt{2}} \qquad b = \frac{1}{\sqrt{2}}}$$

$$E_{+/-} = \varepsilon + 2J\left(\pm\frac{1}{\sqrt{2}}\right)\sqrt{1-\frac{1}{2}} = \varepsilon \pm 2J\frac{1}{2}$$

$$\boxed{E_{+/-} = \varepsilon \pm J}$$

<u>P_a^c</u>

$$H = \begin{pmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{pmatrix}$$

$$|\psi\rangle = \cos\varphi|1\rangle + \sin\varphi|2\rangle = \begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix}$$

$$E_{var} = (\cos\varphi\ \sin\varphi)\begin{pmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{pmatrix}\begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix} =$$

$$= (\cos\varphi\ \sin\varphi)\begin{pmatrix} \varepsilon_1\cos\varphi + J\sin\varphi \\ J\cos\varphi + \varepsilon_2\sin\varphi \end{pmatrix}$$

$$= \varepsilon_1 \cos^2\varphi + J\cos\varphi\sin\varphi + J\sin\varphi\cos\varphi + \varepsilon_2\sin^2\varphi$$

$$= \varepsilon_1 \cos^2\varphi + \varepsilon_2\sin^2\varphi + 2J\cos\varphi\sin\varphi \Rightarrow \frac{\partial}{\partial\varphi}E_{var} = 0$$

$$-2\varepsilon_1\sin\varphi\cos\varphi + 2\varepsilon_2\cos\varphi\sin\varphi + 2J\cos^2\varphi - 2J\sin^2\varphi = 0$$

$$2(\varepsilon_2-\varepsilon_1)\cos\varphi\sin\varphi + 2J(\cos^2\varphi - \sin^2\varphi) = 0$$

$$(\varepsilon_2-\varepsilon_1)\sin 2\varphi + 2J\cos 2\varphi = 0$$

$$\tan 2\varphi = \frac{2J}{\varepsilon_2-\varepsilon_1}$$

pozn.: chyba ve videu

$$\boxed{\varphi = \frac{1}{2}\arctan\left(\frac{2J}{\varepsilon_2-\varepsilon_1}\right)}$$

Přibližná energie základního stavu atomu vodíku

Přibližná vlnová funkce: gaussián $\Psi(r) = N e^{-\alpha r^2}$

Hamiltonián atomu vodíku

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = E_{var}$$

$$\int_0^\infty dr\, r^{2m} e^{-\beta r^2} = \frac{(2m)!\sqrt{\pi}}{2^{2m+1} m!\, \beta^{m+\frac{1}{2}}}$$

$$\int_0^\infty dr\, r^{2m+1} e^{-\beta r^2} = \frac{m!}{2\beta^{m+1}}$$

$$\langle\psi|\psi\rangle = \int_0^\infty dr\, r^2 |\psi(r)|^2$$

$$\nabla^2 e^{-\alpha r^2} = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) e^{-\alpha r^2} = \frac{2}{r}(-2\alpha r) e^{-\alpha r^2} + (-2\alpha) e^{-\alpha r^2}$$

$$+ (-2\alpha r)(-2\alpha r) e^{-\alpha r^2}$$

$$= 4\alpha\left(\alpha r^2 e^{-\alpha r^2} - e^{-\alpha r^2} - \frac{1}{2} e^{-\alpha r^2}\right)$$

$$= 4\alpha\left(\alpha r^2 - \frac{3}{2}\right) e^{-\alpha r^2}$$

$$\frac{1}{2} N e^{-\alpha r^2} \nabla^2 N e^{-\alpha r^2} = N^2 2\alpha \left(\alpha r^2 - \frac{3}{2}\right) e^{-2\alpha r^2}$$

$$\langle\psi|\hat{H}|\psi\rangle = \int_0^\infty dr\, r^2 \left[-N^2 2\alpha\left(\alpha r^2 - \frac{3}{2}\right) e^{-2\alpha r^2} - N \frac{1}{r} e^{-2\alpha r^2} \right]$$

$$= -N^2 2\alpha^2 \int_0^\infty dr\, r^4 e^{-2\alpha r^2} + N^2 3\alpha \int_0^\infty dr\, r^2 e^{-2\alpha r^2} - N^2 \int_0^\infty dr\, r e^{-2\alpha r^2}$$

$$= -N^2 2\alpha^2 \frac{4!\sqrt{\pi}}{2^5\, 2!\,(2\alpha)^{5/2}} + N^2 3\alpha \frac{2!\sqrt{\pi}}{2^3 (2\alpha)^{1/2}} - \frac{N^2}{4\alpha}$$

$$\langle\psi|\psi\rangle = N^2 \int_0^\infty dr\, r^2 e^{-2\alpha r^2} = N^2 \frac{2!\sqrt{\pi}}{2^3 (2\alpha)^{1/2}}$$

$$E = -\frac{\cancel{N^2}\,\cancel{2}\alpha^2\, \cancel{4}\cdot 3\cdot \cancel{2}\,\cancel{\sqrt{\pi}}}{\cancel{2^5}\,\cancel{2}\,(2\alpha)^{3/\cancel{2}}} \cdot \frac{\cancel{2^3}\,\cancel{(2\alpha)^{1/2}}}{\cancel{N^2}\,\cancel{2}\,\cancel{\sqrt{\pi}}} + 3\alpha - \frac{1}{\cancel{4}\alpha} \frac{\cancel{2^3}(2\alpha)^{\cancel{3/2}\ 1/2}}{\cancel{2}\sqrt{\pi}}$$

$$= -\frac{3\alpha^2}{2\alpha} + 3\alpha - \frac{2\sqrt{2}\,\alpha^{1/2}}{\sqrt{\pi}} = -\frac{3}{2}\alpha + \frac{6}{2}\alpha - 2\sqrt{\frac{2\alpha}{\pi}} \Rightarrow$$

$$\Rightarrow E = \frac{3}{2}\alpha - 2\sqrt{\frac{2\alpha}{\pi}}$$

$$\frac{\partial}{\partial\alpha}E = 0 \quad = \frac{3}{2} - 2\,\frac{1}{2}\,\frac{\frac{2}{\pi}}{\sqrt{\frac{2\alpha}{\pi}}} = 0 \quad \Rightarrow \sqrt{\frac{2}{\pi}}\,\frac{1}{\sqrt{\alpha}} = \frac{3}{2} \quad \Big/^2$$

$$\frac{2}{\pi\alpha} = \frac{9}{4} \rightarrow$$

$$\boxed{\alpha = \frac{8}{9\pi}}$$

$$E_g = \frac{3}{2}\,\frac{8}{9\pi} - 2\sqrt{\frac{2\cdot 8}{9\pi^2}} = \frac{12}{9\pi} - 2\,\frac{4}{3\pi} = \frac{12}{9\pi} - \frac{24}{9\pi} = -\frac{12}{9\pi} = -\frac{4}{3\pi}$$

$$E_g = -0{,}4244$$

Exaktní výsledek je $E_{gH} = -\frac{1}{2}$ ← v atomových jednotkách