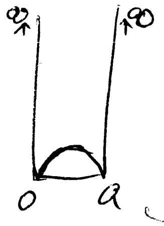
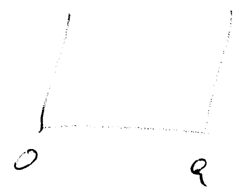
2 1.8 Potenciálová jáma

1.) 

$\psi = N x(a-x)$ (approx.)

$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$, $n = 1, 2, 3 \dots$ (exact)



normování ? c_n , ? $\langle E \rangle$, ? $\langle (\Delta E)^2 \rangle$

$$1 = \langle \psi | \psi \rangle = N^2 \int_0^a x^2 (a-x)^2 \, dx = N^2 \int_0^a x^2 (x^2 - 2ax + a^2) \, dx =$$

$$= N^2 \int_0^a (x^4 - 2ax^3 + a^2 x^2) \, dx = N^2 \left[\frac{x^5}{5} - \frac{2ax^4}{4} + \frac{a^2 x^3}{3} \right]_0^a$$

$$= N^2 \left[\frac{a^5}{5} - \frac{a^5}{2} + \frac{a^5}{3} \right] = N^2 a^5 \left[\frac{6 - 15 + 10}{30} \right] = \frac{N^2 a^5}{30} = 1$$

$$\Rightarrow N^2 = \frac{30}{a^5} \quad ; \quad N = \sqrt{\frac{30}{a^5}} \quad \text{ok}$$

$\pm$ actually...

$$1 = \langle \psi_n | \psi_n \rangle = \frac{2}{a} \int_0^a \sin^2 \frac{n\pi x}{a} \, dx = \frac{2}{a} \cdot \left[x \cdot 1/2 \right]_0^a = \frac{2}{a} \cdot \frac{a}{2} = 1 \quad \text{ok}$$

$$c_n = \langle \psi_n | \psi \rangle = \sqrt{\frac{30}{a^5}} \sqrt{\frac{2}{a}} \int_0^a \sin \frac{\pi n x}{a} \cdot x(a-x) \, dx$$

$$= \frac{2\sqrt{15}}{a^3} \int_0^a \left[ax \sin \frac{\pi n x}{a} - x^2 \sin \frac{\pi n x}{a} \right] dx = \ast$$

$b = \frac{\pi n}{a}$

$$\int_0^a x \sin bx \, dx = -\int_0^a \frac{d}{dx} \left[\frac{x}{b} \cos bx \right] dx + \int_0^a \frac{\cos bx}{b} \, dx = -\left[\frac{x}{b} \cos bx \right]_0^a + \left[\frac{\sin bx}{b^2} \right]_0^a$$

$$= -\left[\frac{xa}{\pi n} \cos \frac{\pi n x}{a} \right]_0^a + \left[\frac{a^2}{\pi^2 n^2} \sin \frac{n\pi x}{a} \right]_0^a$$

$$= -\left[\frac{a^2}{\pi n} \cos(n\pi) - 0 \right] + \left[0 - 0 \right] = -\frac{a^2}{\pi n} \cos(n\pi)$$

$$\int_0^a x^2 \sin \underbrace{\frac{n\pi x}{a}}_{b} \, dx = \int_0^a x^2 \sin bx \, dx \overset{\text{p.p. } 2x}{=} \left[\underbrace{\frac{2x}{b^2} \sin(bx)}_{0} - \frac{(x^2 b^2 - 2) \cos(bx)}{b^3} \right]_0^a$$

$$= -\left[\frac{\left(x^2 \frac{\pi^2 n^2}{a^2} - 2 \right) \cos\left(\frac{n\pi x}{a} \right)}{\frac{\pi^3 n^3}{a^3}} \right]_0^a = -\left[\frac{(\pi^2 n^2 - 2) \cos(n\pi)}{\frac{\pi^3 n^3}{a^3}} - \frac{-2 \cos(0)}{\frac{\pi^3 n^3}{a^3}} \right]$$

$$= \frac{a^3}{\pi^3 n^3} \left[(-\pi^2 n^2 + 2) \cos(n\pi) - 2 \right]$$

$$* = c_n = \langle \psi_n | \psi \rangle = \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{\pi n}\cos(n\pi) - \frac{a^3}{\pi^3 n^3}\left[(2-\pi^2 n^2)\cos(n\pi) - 2\right]\right]$$

$$= \frac{2\sqrt{15}}{a^3} a^3 \left[-\frac{1}{\pi n}\cos(n\pi) + \frac{2}{\pi^3 n^3} + \frac{\cos(n\pi)}{\pi n} - \frac{2\cos(n\pi)}{\pi^3 n^3}\right]$$

$$= 2\sqrt{15} \cdot 2 \cdot \left[\frac{1-\cos(n\pi)}{\pi^3 n^3}\right]$$

pro $n = 1, 3, 5, \ldots \Rightarrow c_n = 4\sqrt{15}\,\frac{2}{\pi^3 n^3}$, pro $n = 1$ $c_1 = 0.999278$.

pro $n = 2, 4, 6, \ldots \Rightarrow c_n = 0$ proč?

$\langle E \rangle$: $\langle \psi | H | \psi \rangle = N^2 \int_0^a x(a-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) x(a-x)\, dx$ D.Ú.

$$\frac{d^2}{dx^2}(xa - x^2) = -2$$

$$= \frac{30}{a^5}\int_0^a (ax - x^2)\left(-\frac{\hbar^2}{2m}\right)(-2)\, dx = \frac{30\hbar^2}{a^5 m}\int_0^a (ax - x^2)\, dx =$$

$$= \frac{30\hbar^2}{a^5 m}\left[\frac{1}{2}ax^2 - \frac{x^3}{3}\right]_0^a = \frac{30\hbar^2}{a^5 m}\left[\frac{1}{2}a^3 - \frac{a^3}{3}\right] = \frac{5\hbar^2}{ma^2}$$

c.f. $E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$

$$\frac{E(\psi)}{E_1} = \frac{\frac{5\hbar^2}{ma^2}}{\frac{\hbar^2\pi^2}{2ma^2}} = \frac{10}{\pi^2} \leftarrow = 9.8696 \Rightarrow E(\psi) = 1.013\, E_1$$

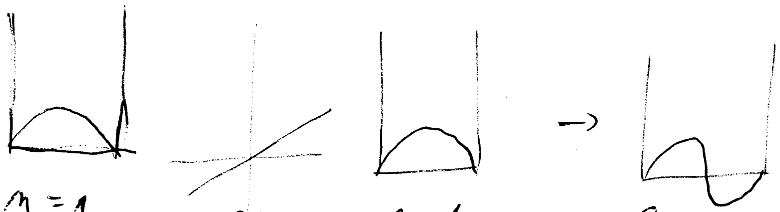
– odhad energií zákl. stavu pomocí zkusmých funkcí: variační metody [Monte Carlo, VMC, QMC] J. Chem. Phys. 140, 174703, 2014 QMC

$\langle H^2 \rangle$ D.Ú.

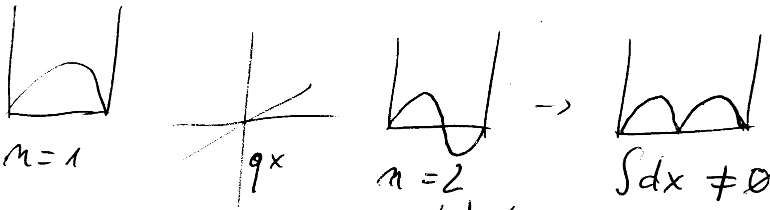
21.8.

3. $\langle m | qx | n \rangle$ - dipólová porucha - el. pole, záření, ...

$$\psi_n : \begin{cases} \psi_n = \sqrt{\frac{2}{a}} \cos \frac{n\pi x}{a}, & n \text{ liché} \\ \psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, & n \text{ sudé} \end{cases}$$



$n = 1$ $\quad$ qx $\quad$ $n = 1$ & liché $\quad$ $\rightarrow$ $\quad$ $\int dx = 0$



$n = 1$ $\quad$ qx $\quad$ $n = 2$ & ostatní sudé $\quad$ $\rightarrow$ $\quad$ $\int dx \neq 0$

$$\underset{m \text{ liché}}{\langle \psi_m} | qx | \underset{n \text{ sudé}}{\psi_n \rangle} = \frac{2q}{a} \int_{-a/2}^{a/2} x \cdot \cos\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx = *$$

$$\cos\left(\frac{m\pi x}{a}\right) = \frac{1}{2}\left[\exp\left(\frac{im\pi x}{a}\right) + \exp\left(-\frac{im\pi x}{a}\right)\right]$$

$$\sin\left(\frac{n\pi x}{a}\right) = \frac{1}{2i}\left[\exp\left(\frac{in\pi x}{a}\right) - \exp\left(-\frac{in\pi x}{a}\right)\right]$$

$$* = \frac{2q}{a} \int_{-a/2}^{a/2} x \left(\frac{1}{2}\right)\left(\frac{1}{2i}\right)\left[\exp\left(\frac{im\pi x}{a}\right) + \exp\left(-\frac{im\pi x}{a}\right)\right]\left[\exp\left(\frac{in\pi x}{a}\right) - \exp\left(-\frac{in\pi x}{a}\right)\right] = **$$

$$\left(e^{im} + e^{-im}\right)\left(e^{in} - e^{-in}\right) = e^{i(m+n)} - e^{i(m-n)} + e^{-i(m-n)} - e^{-i(m+n)}$$

$$= e^{i(m+n)} - e^{-i(m+n)} + e^{-i(m-n)} - e^{i(m-n)}$$

$$= (2i)\left[\sin(m+n) - \sin(m-n)\right]$$

$$** = \frac{2q}{a} \int_{-a/2}^{a/2} x \left(\frac{1}{2}\right)\left[\sin\left(\frac{(m+n)\pi x}{a}\right) - \sin\left(\frac{(m-n)\pi x}{a}\right)\right]$$

$$= \frac{q}{a} \int_{-a/2}^{a/2} x \left[\sin\left(\frac{(m+n)\pi x}{a}\right) - \sin\left(\frac{(m-n)\pi x}{a}\right)\right] = ***$$

$$\int_{-a/2}^{a/2} x \sin bx = -\left[\frac{x}{b}\cos bx\right]_{-a/2}^{a/2} + \left[\frac{\sin bx}{b^2}\right]_{-a/2}^{a/2}$$

T3 - 2a

$$\int_{-a/2}^{a/2} x \sin bx = -\left[\frac{x}{b}\cos(bx)\right]_{-a/2}^{a/2} + \left[\frac{\sin(bx)}{b^2}\right]_{-a/2}^{a/2} =$$

$$\left(b_1 = \frac{(m+n)\pi}{a}\right) \quad = -\left[\frac{xa}{(m+n)\pi}\cos\left(\frac{(m+n)\pi x}{a}\right)\right]_{-a/2}^{a/2} + \left[\frac{a^2}{(m+n)^2\pi^2}\sin\left(\frac{(m+n)\pi x}{a}\right)\right]_{-a/2}^{a/2} =$$

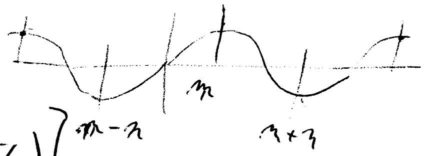
$$\Downarrow \quad \cos\big(\underbrace{(m+n)}_{\text{liché}}\tfrac{\pi}{2}\big) = 0$$

$$= \frac{a^2}{(m+n)^2\pi^2}\left[\sin\left((m+n)\frac{\pi}{2}\right) - \sin\left[(m+n)\left(-\frac{\pi}{2}\right)\right]\right]$$

$$= \frac{2a^2}{(m+n)^2\pi^2}\sin\left((m+n)\frac{\pi}{2}\right)$$

rozdíl také lichý

$$b_2 = \frac{(m-n)\pi}{a} \rightarrow \frac{2a^2}{(m-n)^2\pi^2}\sin\left((m-n)\frac{\pi}{2}\right)$$



$$*** = \frac{q}{a}\left[\frac{2a^2}{(m+n)^2\pi^2}\sin\left((m+n)\frac{\pi}{2}\right) - \frac{2a^2}{(m-n)^2\pi^2}\sin\left((m-n)\frac{\pi}{2}\right)\right]$$

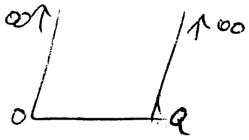
$$\sin\left((m+n)\frac{\pi}{2}\right) = \sin\left((m-n)\frac{\pi}{2}\right)$$

$$= \frac{2aq}{\pi^2}\sin\left((m+n)\frac{\pi}{2}\right)\left[\frac{1}{(m+n)^2} - \frac{1}{(m-n)^2}\right]$$

$$= \frac{2aq}{\pi^2}\sin\left((m+n)\frac{\pi}{2}\right)\left[\frac{m^2-2mn+n^2-m^2-2mn-n^2}{(m^2-n^2)^2}\right]$$

$$= \frac{-8aqmn}{\pi^2}\sin\left((m+n)\frac{\pi}{2}\right)\frac{1}{(m^2-n^2)^2} \qquad \text{OK}$$

? x^2 ? p_x D.Ú.

218.4  časový vývoj 

$$\psi = N\left(\sin\frac{\pi x}{a} + \sin\frac{2\pi x}{a}\right)$$

, střední hodnota x

normalisace:

$$1 = \langle\psi|\psi\rangle = N^2\int_0^a \left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right]\left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right]dx$$

$$= N^2\int_0^a \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + 2\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\right]dx$$

$= 0$ [vypočtěte!]

$$= N^2\int_0^a \left[a/2 + a/2\right] = N^2 a = 1$$

$$N^2 = \frac{1}{a}$$

$$\psi(x,0) = \frac{1}{\sqrt{a}}\left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right] \quad \text{OK}$$

čas $t_0 = 0$

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n e^{-iE_n t/\hbar}\psi_n(x,t) \qquad E_n = \frac{\hbar^2\pi^2 n^2}{2ma^2} \qquad \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{a}\right)\right]$$

$$\psi(x,t) = \frac{1}{\sqrt{a}}\left[\sin\left(\frac{\pi x}{a}\right)e^{-\frac{i\hbar\pi^2}{2ma^2}t} + \sin\left(\frac{2\pi x}{a}\right)e^{-\frac{4i\hbar\pi^2}{2ma^2}t}\right]$$

normování - zachováno $\left(e^{-i\frac{E_n}{\hbar}t}\right)^* e^{-iE_n t/\hbar} = 1$ $\quad\langle\psi(t)|\psi(t)\rangle = 1$

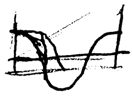
$$\langle\psi|x|\psi\rangle = \int_0^a \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

$$= \frac{1}{a}\int_0^a \left[\sin\left(\frac{\pi x}{a}\right)e^{+iE_1 t/\hbar} + \sin\left(\frac{2\pi x}{a}\right)e^{+iE_2 t/\hbar}\right] x \left[\sin\left(\frac{\pi x}{a}\right)e^{-iE_1 t/\hbar} + \sin\left(\frac{2\pi x}{a}\right)e^{-iE_2 t/\hbar}\right]dx =$$

$$= \frac{1}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right) + x\sin^2\left(\frac{2\pi x}{a}\right) + x\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)\left[e^{i(E_1-E_2)t/\hbar} + e^{-i(E_1-E_2)t/\hbar}\right]$$

$$\frac{1}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right) = \frac{1}{a}\int_0^a x\left[\left(\frac{1}{2i}\right)^2\left(\exp\left(\frac{i\pi x}{a}\right) - \exp\left(-\frac{i\pi x}{a}\right)\right)^2\right] = -\frac{1}{4a}\int_0^a x\left[\exp\left(\frac{2i\pi x}{a}\right) + \exp\left(-\frac{2i\pi x}{a}\right) - 2\right]$$

$$= -\frac{1}{4a}\int_0^a x\,2\left[\frac{1}{2}\left(\exp\left(\frac{2i\pi x}{a}\right) + \exp\left(-\frac{2i\pi x}{a}\right)\right) - 1\right] = -\frac{1}{2a}\int_0^a x\left[\cos\left(\frac{2\pi x}{a}\right) - 1\right]dx$$

$$= \int_0^a \frac{x}{2a}dx - \frac{1}{2a}\int_0^a x\cos\left(\frac{2\pi x}{a}\right)dx = \left[\frac{x^2}{4a}\right]_0^a - \frac{1}{2a}\int_0^a x\cos\left(\frac{2\pi x}{a}\right)dx$$ 

$$\int_0^a x\cos\left(\frac{2\pi x}{a}\right) = \left[\frac{ax\sin\frac{2\pi x}{a}}{2\pi}\right]_0^a + \left[\frac{a^2}{4\pi^2}\cos\left(\frac{2\pi x}{a}\right)\right]_0^a = 0$$

$$= \frac{a}{4}$$, stejně pro $\frac{1}{a}\int_0^a x\sin^2\left(\frac{2\pi x}{a}\right) = \frac{a}{4}$

$$\frac{1}{a}\int_0^a x \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right) \cdot f(t) =$$

$$f(t) = e^{i(E_1-E_2)t/\hbar} + e^{-i(E_1-E_2)t/\hbar} = 2\cos[(E_1-E_2)t/\hbar]$$

$$= \frac{1}{2a}\int_0^a x\left[\cos\left(\frac{\pi x}{a}\right) - \cos\left(\frac{3\pi x}{a}\right)\right] dx \; f(t) = *$$

$$2\sin(\alpha)\sin(\beta) = \cos(\alpha-\beta) - \cos(\alpha+\beta)$$

$$\int_0^a x\cos\left(\frac{\pi x}{a}\right)dx = \left[\frac{ax\sin\left(\frac{\pi x}{a}\right)}{\pi}\right]_0^a + \left[\frac{a^2}{\pi^2}\cos\left(\frac{\pi x}{a}\right)\right]_0^a = \frac{a^2}{\pi^2}[-1-1] = -\frac{2a^2}{\pi^2}$$

almost same for $\cos\left(\frac{3\pi x}{a}\right) \to -\frac{2a^2}{9\pi^2}$

$$\frac{1}{a}\left[-\frac{2a^2}{\pi^2} + \frac{2a^2}{9\pi^2}\right] = 2a\left[-\frac{1}{\pi^2} + \frac{1}{9\pi^2}\right] = -\frac{16a}{9\pi^2}$$

$$\Rightarrow * = \frac{1}{2}\cdot\left(-\frac{16a}{9\pi^2}\right) 2\cos[(E_1-E_2)t/\hbar] = -\frac{16a}{9\pi^2}\cos[(E_1-E_2)t/\hbar]$$

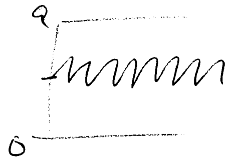
celkem

$$\langle x\rangle = \frac{a}{4} + \frac{a}{4} - \frac{16a}{9\pi^2}\cos[(E_1-E_2)t/\hbar] =$$

$$= \frac{a}{2} + \frac{16a}{9\pi^2}\cos[(E_1-E_2)t/\hbar]$$

$\doteq \frac{16}{84} \doteq \frac{4}{21} \doteq 0.2$

OK

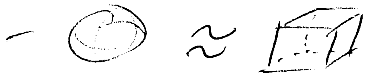


– pro $\psi = \frac{1}{\sqrt{2}}[\psi_1 + \psi_3]$?

$\psi = \frac{1}{\sqrt{2}}[\psi_1 + \psi_4]$?

amplituda ?
0.Ú.

Q d

-  $E_n = \frac{\hbar^2 \pi^2 n^2}{2 m a^2}$

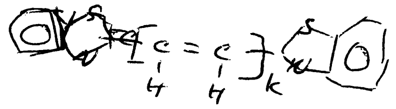
$a = 23 Å$ assume $1 \to 2$ transition

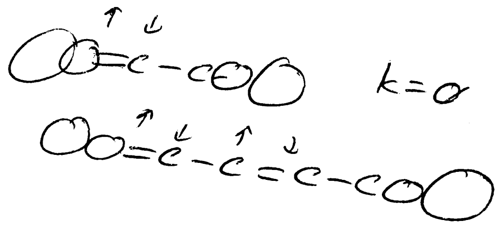
$E_n = \frac{\pi^2 n^2}{2a^2} = \frac{\pi^2 n^2}{2 \cdot 44^2} = 0.00255\ Ha$ ~ ~~[illegible]~~

hm... actually more gap dependent...

---

polyenes - paper by Autschbach



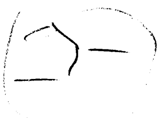


$k=0$

$k=1$

⋮

$\boxed{-C=C-}$ with H, H



~~a = 240 pm~~

$a = 250 pm$ ≙ 4.7 ~~25~~ B

extra space

$b = 550 pm$ ≙ $10.4 B$

$L = a(k+1) + b$

$E_n = \frac{\hbar^2 \pi^2 n^2}{2 m_e L^2}$

$k=0$ $k=1$ $k=2$

! actually $>\ddot{N} - \underset{H}{C} = \underset{H}{C} - [\underset{H}{C} = \underset{H}{C}]_k - \underset{H}{C} = N^+ <$

$k = 0$ 3π-conjugated pairs, $3+k$ generally...

	# pairs	← is HOMO level
$k=0$	→ 3	← $= 3+k$
1	→ 4	
2	→ 5...	

~~[illegible]~~ $E_{HOMO} = \frac{\hbar^2 \pi^2 n^2}{2 m_e L^2} = \frac{\hbar^2 \pi^2 (3+k)^2}{2 m_e [a(k+1)+b]^2}$ ≈ const

$E_{LUMO} = \frac{\hbar^2 \pi^2 (4+k)^2}{2 m_e [a(k+1)+b]^2}$

$E_{LUMO} - E_{HOMO} = \frac{\hbar^2 \pi^2}{2 m_e [a(k+1)+b]^2} [(4+k)^2 - (3+k)^2] = \frac{\hbar^2 \pi^2 [7+2k]}{2 m_e [a(k+1)+b]^2} \approx \frac{1}{k}$

$k=0$: $\frac{\pi^2\, 7}{2[a+b]^2} ≙ \frac{7\pi^2}{2 \cdot 15^2} = 0.1535\ Ha$ ≙ 300 nm expt = 313 nm

$$E_{n+1} - E_{n} = \frac{\hbar^2 \pi^2 \,(7+2k)}{2m_e^2 \left[a(k+1)+b\right]^2} \qquad \text{in a.u. } \frac{\pi^2(7+2k)}{2\left[a(k+1)+b\right]^2}$$

$c = 137$ [a.u.]

$a = 4.7B \quad b = 10.4B$

$$\Delta E = \hbar\omega = \hbar 2\pi \nu = 2\pi\hbar \frac{c}{\lambda} \rightsquigarrow \frac{137 \cdot 2\pi}{\lambda} \text{ [a.u.]}$$

$$\lambda = \frac{137 \cdot 2\pi}{\Delta E} \text{ [a.u.]}$$

$1.\,B = 0.529\,\text{Å} = 0.0529\,nm$

$$\lambda = \frac{137 \cdot 2\pi}{\Delta E} \cdot 0.0529\,nm = \frac{45.54}{\Delta E}\,nm$$

k	n_{Homo}	Exp	calc ues ΔE	λ
0	3	313	0.1515	309
1	4	416	0.1133	402
2	5	519	0.0904	504
3	6	625	0.0752	606

approx linear

ΔE in Ha (a.u.)

ΔE in eV:

$$\frac{45.54}{\Delta E[Ha]} = \frac{45.54}{\Delta E\, 27.2116[eV]} = \frac{\cancel{1.674}\ 1239}{\Delta E\,[eV]}$$