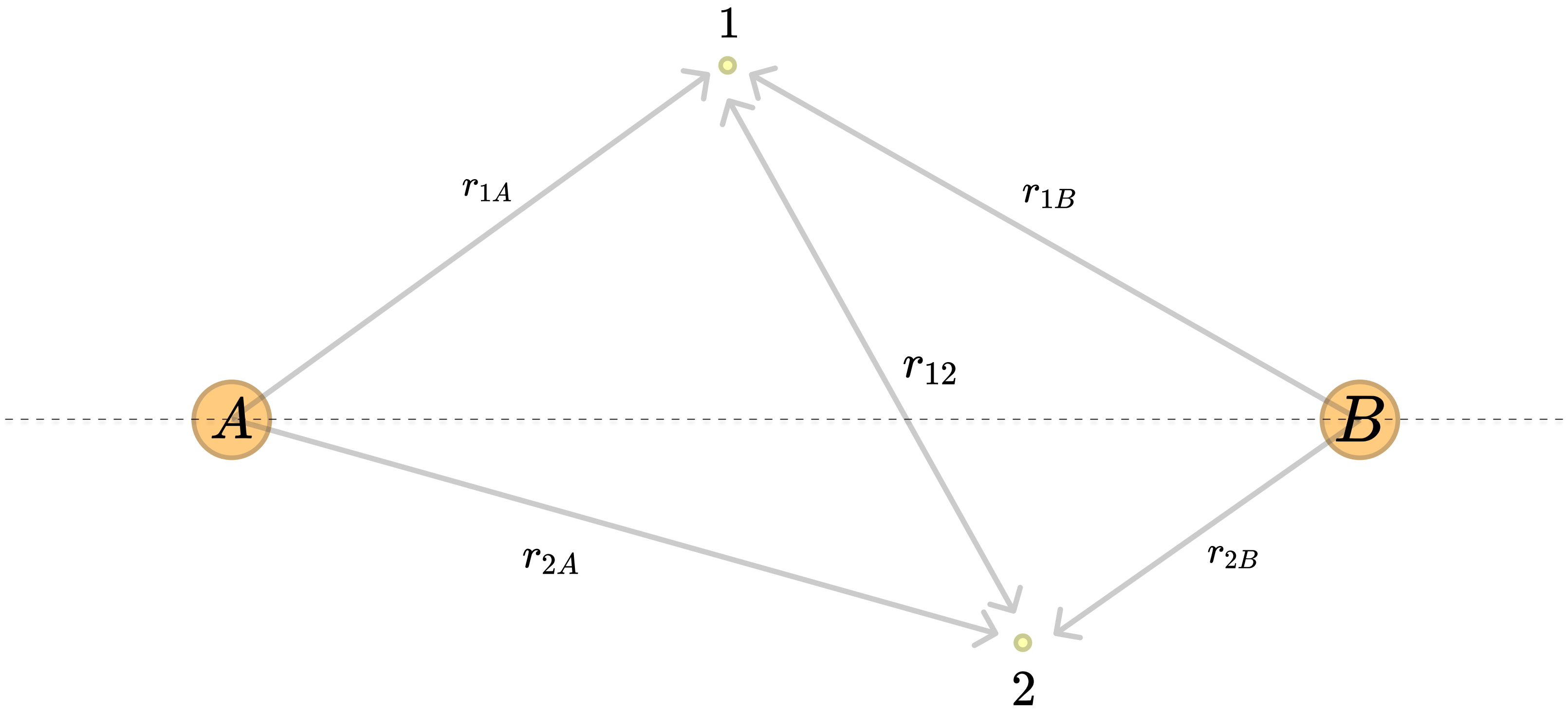
Obliczenia elektrycznych momentów dipolowych dla dwuelektronowych dwuatomowych cząsteczek

Wojciech Noskowiak

Funkcje Kołosa-Woloniewicza



$$\phi(r, n_0, n_1, n_2, n_3, n_4) = e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-v(r_{2A}+r_{2B})}$$

$$r_{12}^{\mathrm{n}_0}(r_{1A} - r_{1B})^{\mathrm{n}_1}(r_{2A} - r_{2B})^{\mathrm{n}_2}\,(r_{1A} + r_{1B})^{\mathrm{n}_3}(r_{2A} + r_{2B})^{\mathrm{n}_4}$$

$$n_0 + n_1 + n_2 + n_3 + n_4 \leq \Omega$$

Dla czego akurat te funkcje?

- Bazę definiuje tylko 5 parametrów, co ułatwia ich optymalizację
- Ma ona ciekawe właściwości znacząco ułatwiające obliczenia

$$f(r, n_0, n_1, n_2, n_3, n_4) = \frac{r_{AB}}{n_0!\, n_1!\, n_2!\, n_3!\, n_4!} \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-x(r_{2A}+r_{2B})}}{r_{12} r_{1A} r_{1B} r_{2A} r_{2B}}$$

$$r_{12}^{\mathrm{n}_0}(r_{1A} - r_{1B})^{\mathrm{n}_1}(r_{2A} - r_{2B})^{\mathrm{n}_2}\ (r_{1A} + r_{1B})^{\mathrm{n}_3}(r_{2A} + r_{2B})^{\mathrm{n}_4}$$

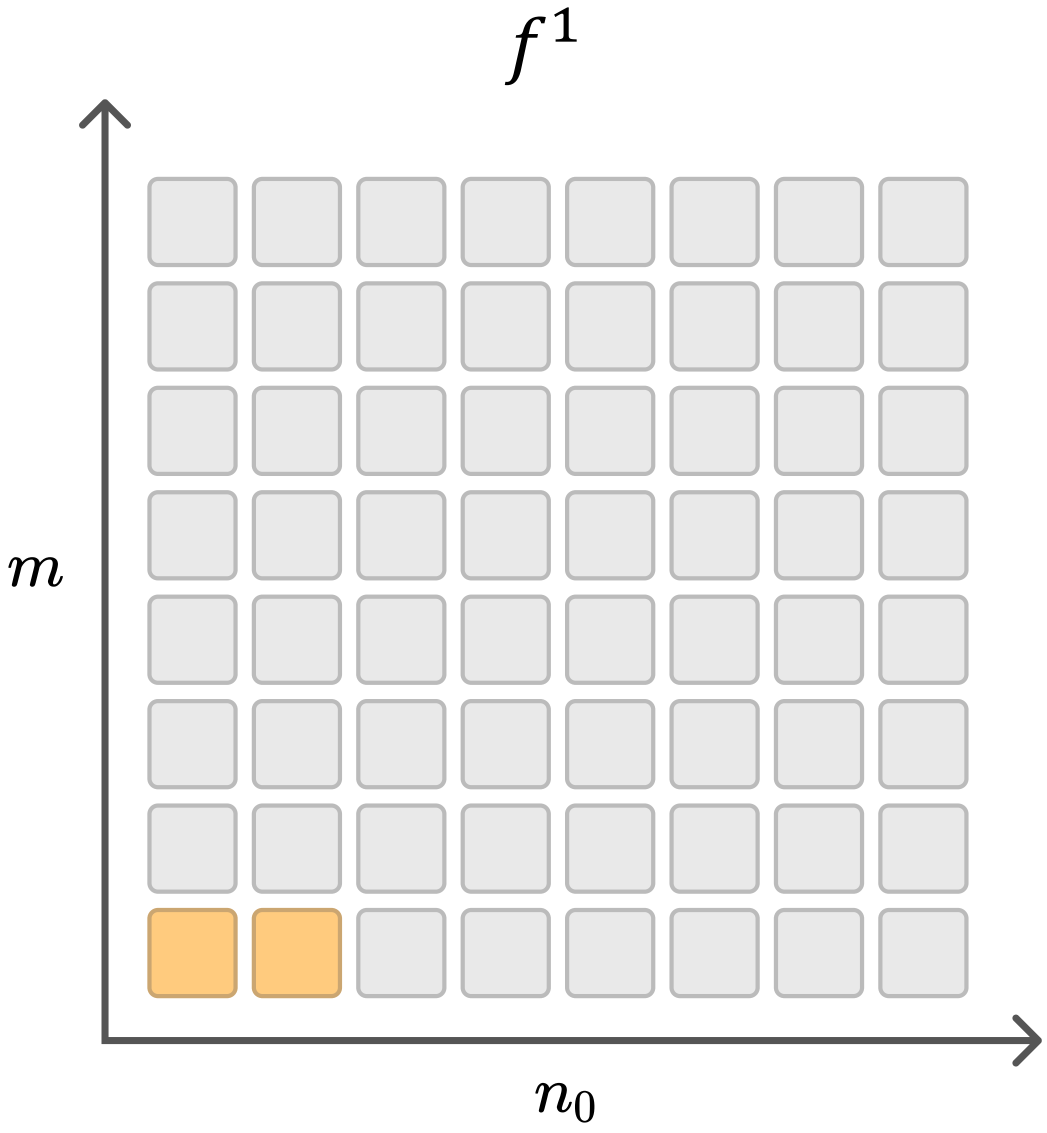
$$f(r,0{,}0{,}0{,}0{,}0) = r\int \frac{d^3r_1}{4\pi}\int \frac{d^3r_2}{4\pi}\frac{e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-x(r_{2A}+r_{2B})}}{r_{12}r_{1A}r_{1B}r_{2A}r_{2B}}$$

$$f(r,n_0,n_1,n_2,n_3,n_4) = \frac{r}{n_0!\,n_1!\,n_2!\,n_3!\,n_4}\left(-\frac{\partial}{\partial w_1}\right)^{n_0}\Bigg|_{w_1=0}\left(-\frac{\partial}{\partial y}\right)^{n_1}\left(-\frac{\partial}{\partial x}\right)^{n_2}\left(-\frac{\partial}{\partial u}\right)^{n_3}\left(-\frac{\partial}{\partial w}\right)^{n_4} f(r)$$

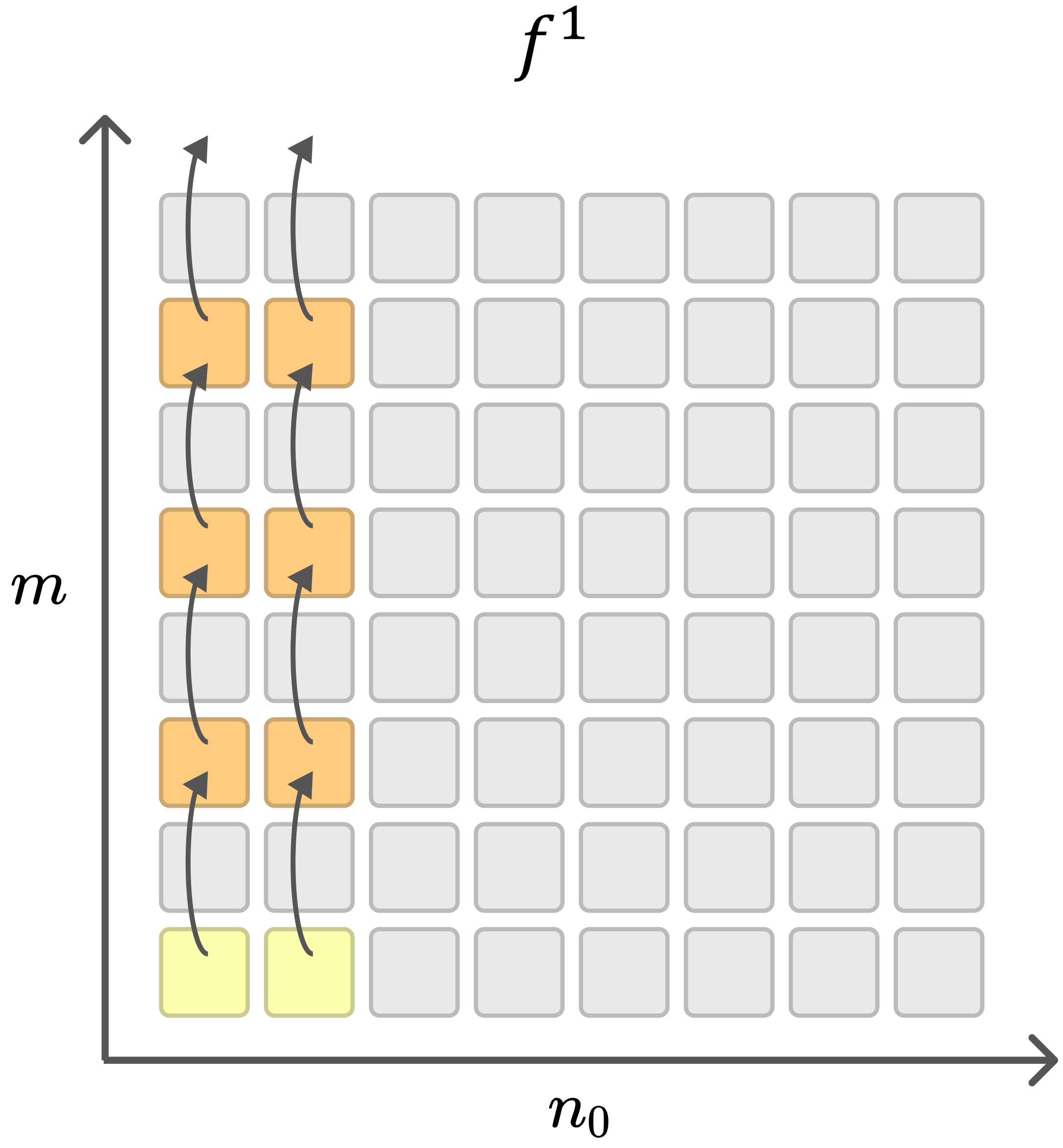
$$\langle k_0, \cdots, k_4 | l_0, \cdots, l_4 \rangle = \frac{1}{16}(f(n_0+1, n_1, n_2, n_3+2, n_4+2) - f(n_0+1, n_1, n_2+2, n_3+2, n_4)$$
$$-f(n_0+1, n_1, n_2+2, n_3, n_4+2) + f(n_0+1, n_1+2, n_2+2, n_3, n_4))$$

$$\begin{aligned}
&\langle k_0, \cdots, k_4 | V | l_0, \cdots, l_4 \rangle \\
&= \frac{1}{16r}(f(n_0, n_1, n_2, n_3+2, n_4+2) - f(n_0, n_1, n_2+2, n_3+2, n_4) - f(n_0, n_1+2, n_2, n_3, n_4+2) \\
&+ f(n_0, n_1+2, n_2+2, n_3, n_4) \\
&+ 2(Z_A+Z_B)[-f(n_0+1, n_1, n_2, n_3+1, n_4+2) - f(n_0+1, n_1, n_2, n_3+2, n_4+1) \\
&+ f(n_0+1, n_1, n_2+1, n_3+, n_4) + f(n_0+1, n_1+2, n_2, n_3, n_4+1)] \\
&+ 2(Z_A-Z_B)[f(n_0+1, n_1, n_2, n_3+1, n_4+2) + f(n_0+1, n_1+1, n_2, n_3, n_4+2) \\
&- f(n_0+1, n_1+1, n_2+2, n_3, n_4) - f(n_0+1, n_1+2, n_2, n_3+1, n_4)] \\
&+ 2Z_A Z_B[f(n_0+1, n_1, n_2, n_3+1, n_4+2) + f(n_0+1, n_1+1, n_2, n_3, n_4+2) \\
&- f(n_0+1, n_1+1, n_2+2, n_3, n_4) - f(n_0+1, n_1+2, n_2, n_3+1, n_4)]
\end{aligned}$$

$$f(r) = \sum_{m=1}^{\infty} [f_m^1(\ln(r) + \gamma_E) + f_m^2] r^m$$

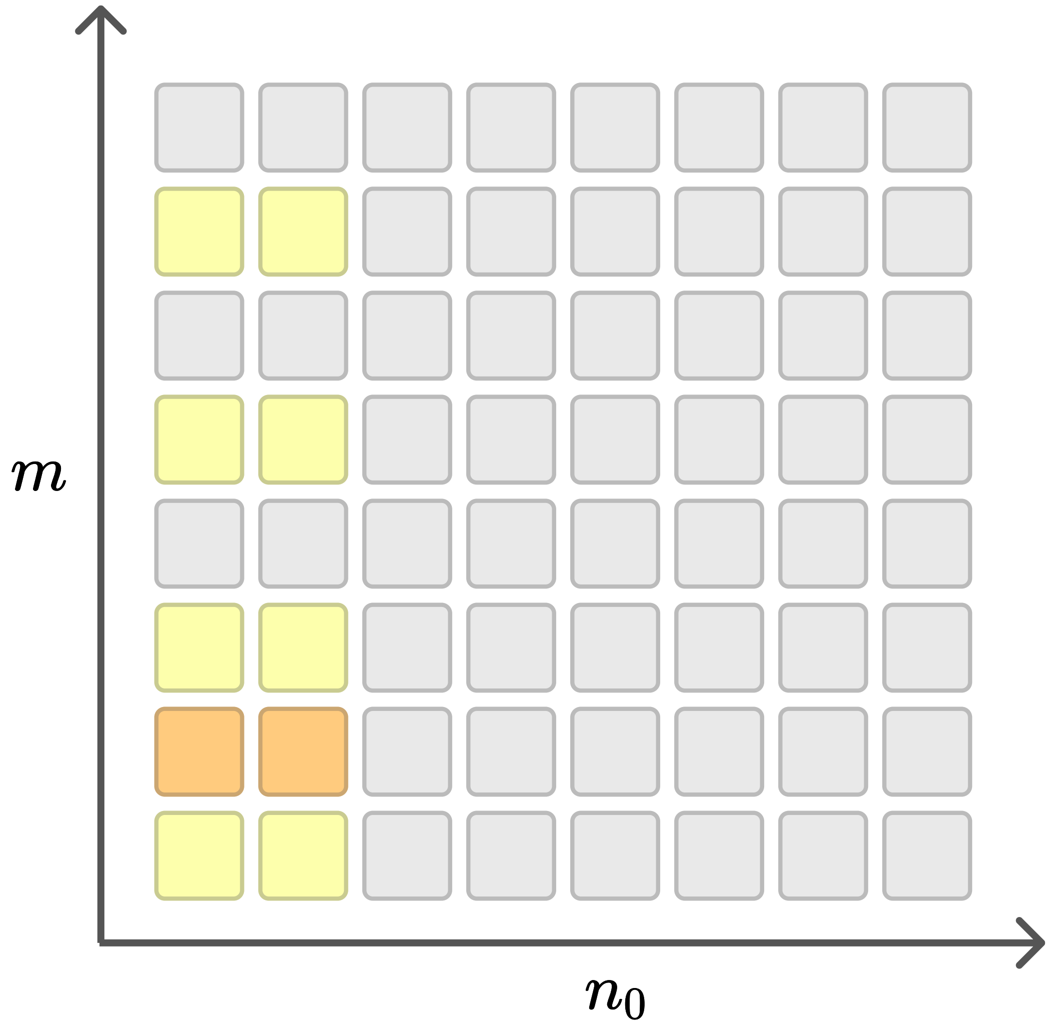


$$n_1 = n_2 = n_3 = n_4 = 0$$

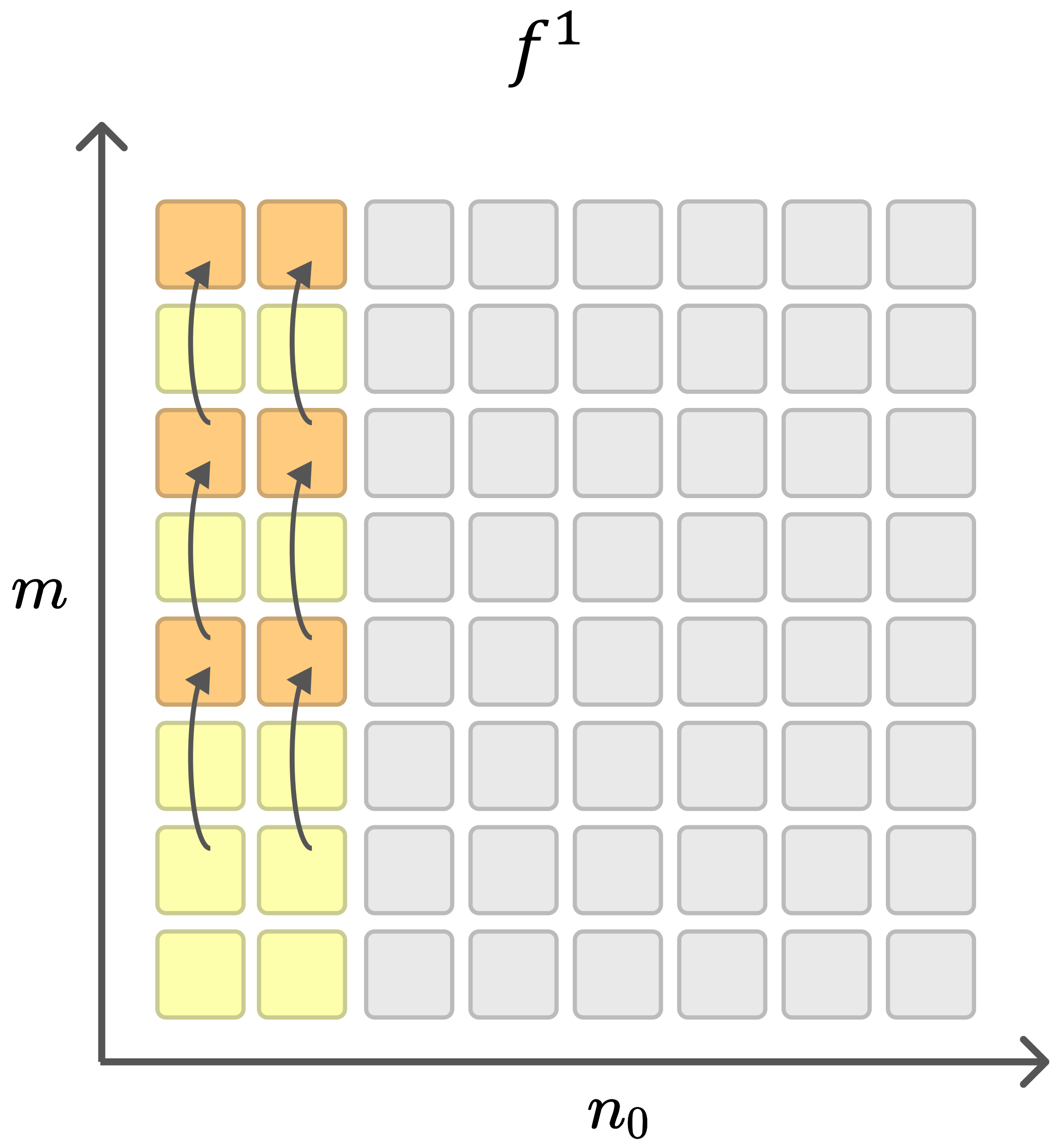


$$n_1 = n_2 = n_3 = n_4 = 0$$

f^1

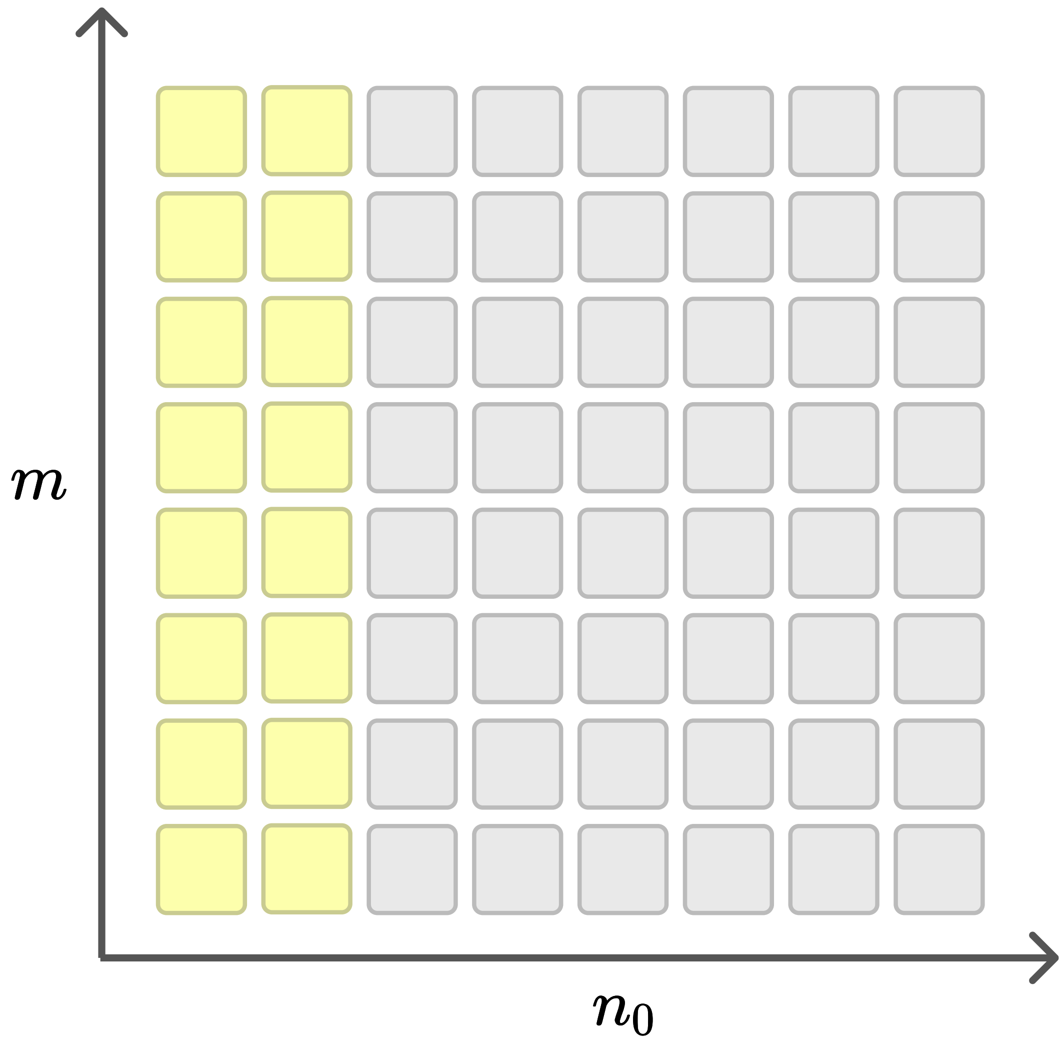


$$n_1 = n_2 = n_3 = n_4 = 0$$



$$n_1 = n_2 = n_3 = n_4 = 0$$

f^1



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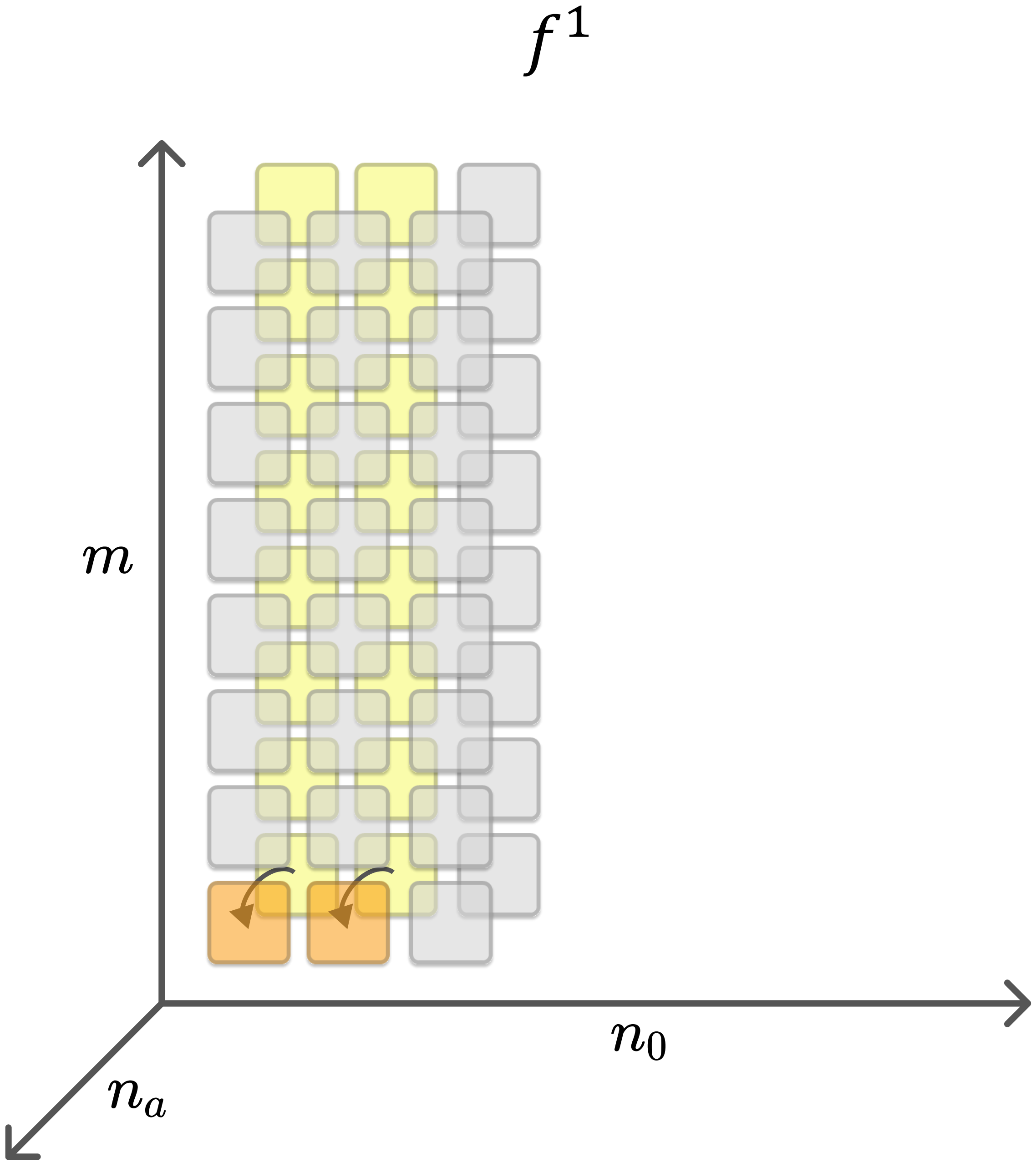
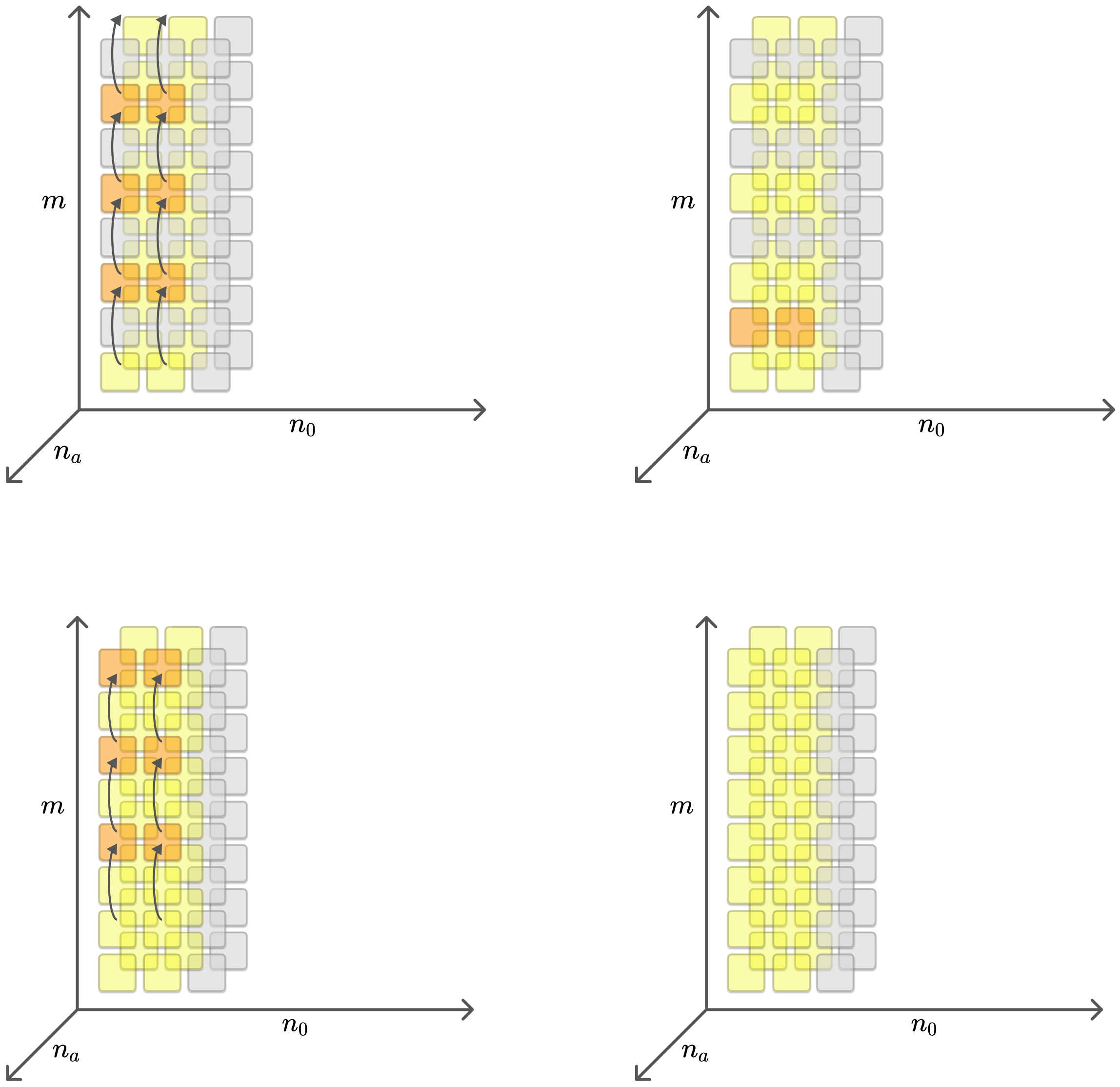
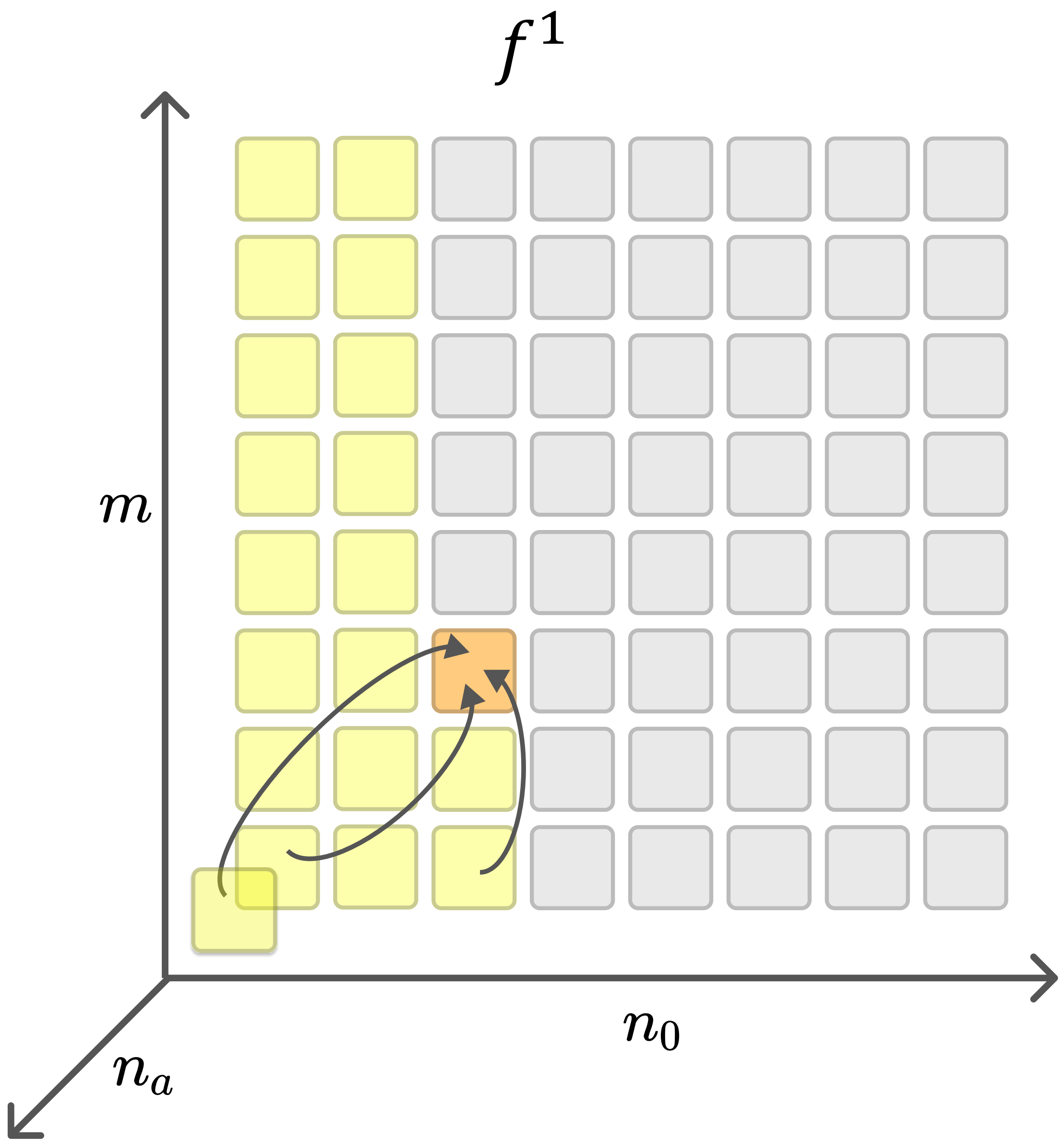


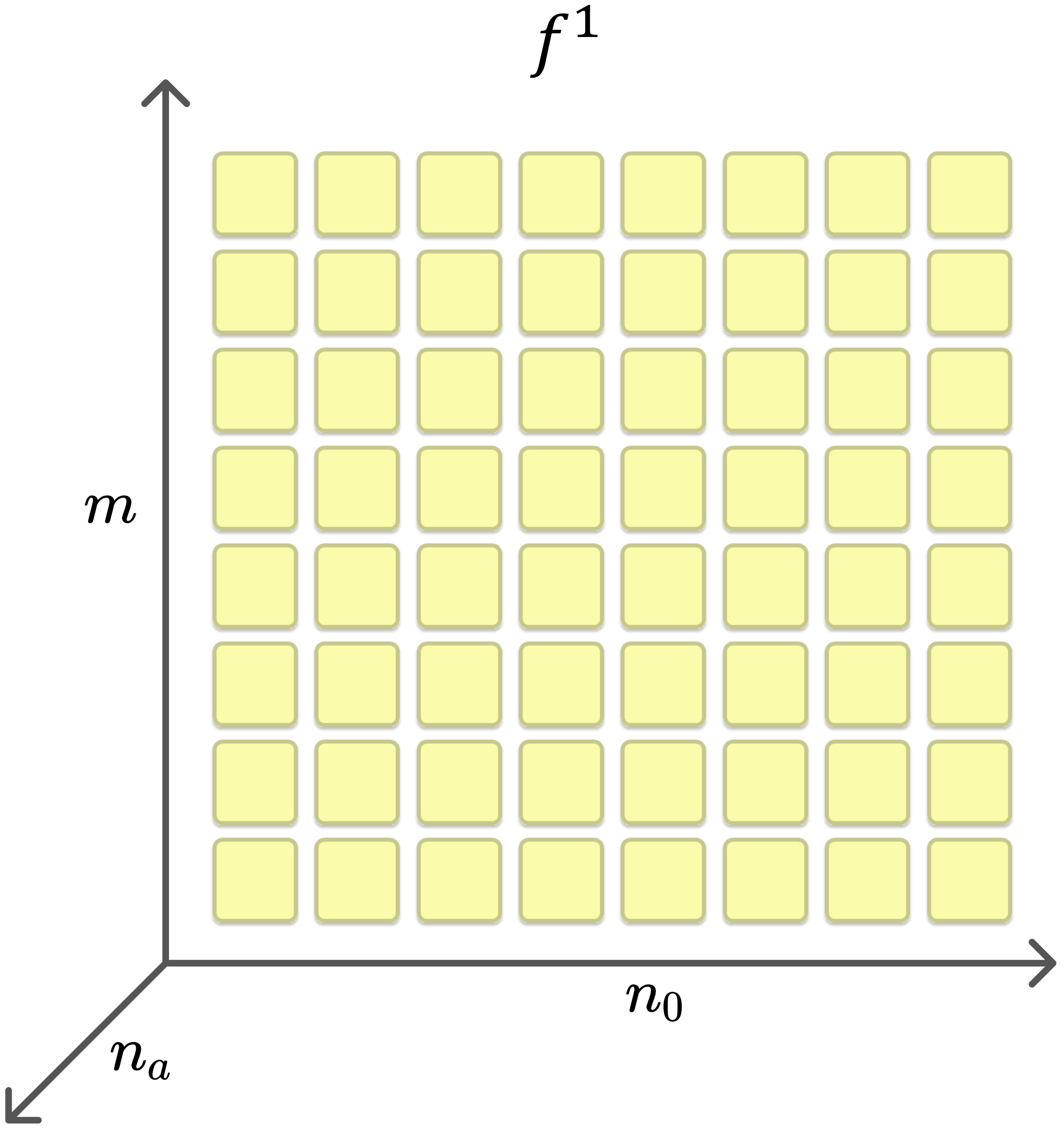
f^1
m
n_0
n_a

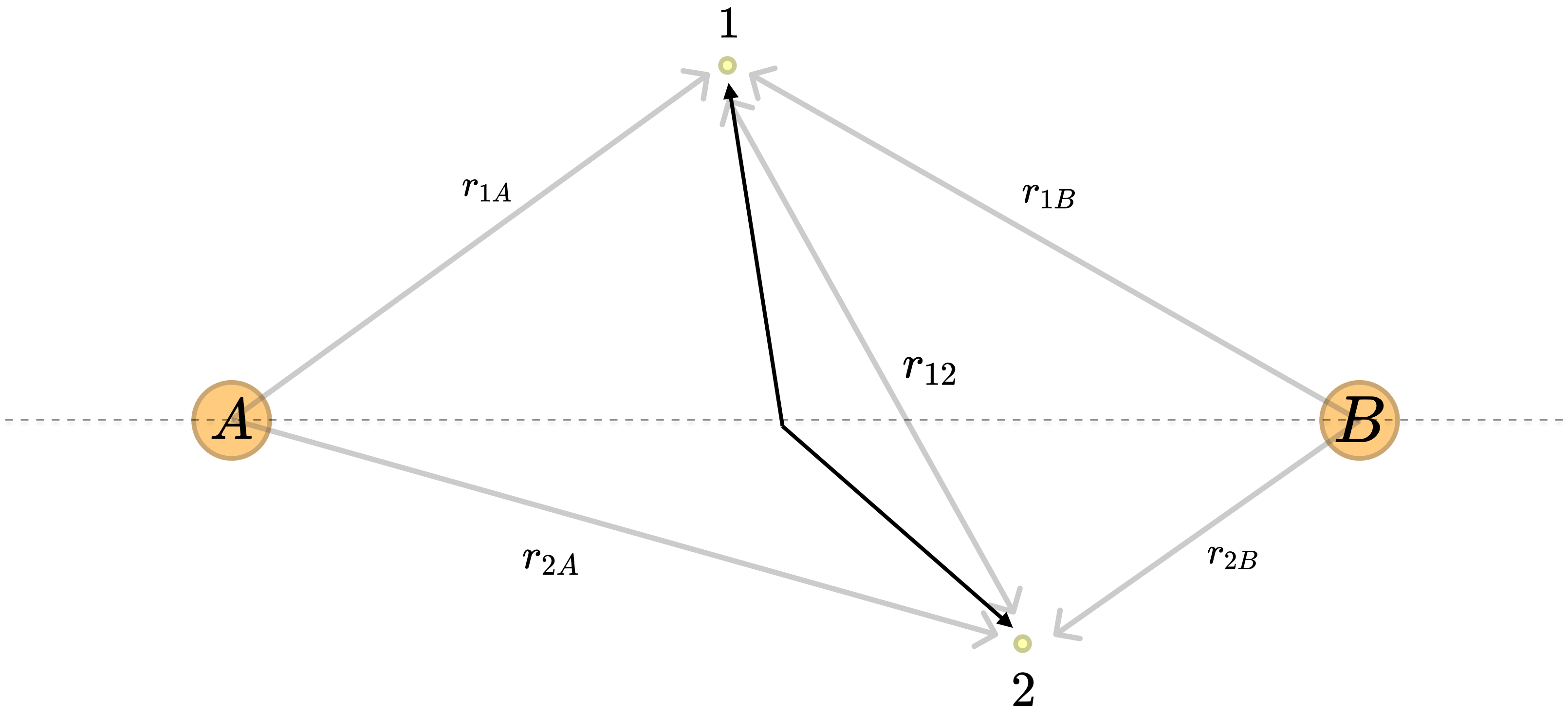
f^1





f^1
m
n_0
n_a


f^1
m
n_0
n_a



$$M = \langle \Psi | r_1 + r_2 | \Phi \rangle$$

Dziękuję