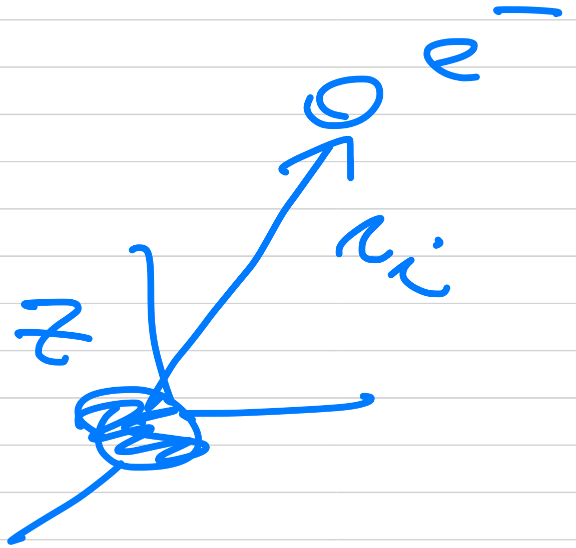
FYS4480/9480 Lecture August 22, 2025

Atomic Helium

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{h}_0(x_i)$$

# of particles

$$\hat{h}_0(x_i) = -\frac{\hbar^2}{2m}\nabla_i^2 + V_{ext}(x_i)$$



$$V_{ext}(r_i) = -\frac{Z}{r_i}$$

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

$$\hat{h}_0(x_i)\,\varphi_{\alpha_j}(x_i) = \varepsilon_{\alpha_j}\,\varphi_{\alpha_j}(x_i)$$

$$\varphi_{\alpha_j}(x_i) = \phi_{\alpha_j}(\vec{r}_i) \otimes \xi^{(i)}_{\sigma_j m_{\sigma_j}}$$

$$\begin{array}{ccc} \begin{bmatrix}1\\0\end{bmatrix} & \vee & \begin{bmatrix}0\\1\end{bmatrix} \\ \uparrow & & \downarrow \end{array}$$

$$\alpha_j = n_j\, l_j\, m_{l_j}$$

$$\phi_{\alpha_j}(\vec{r}_i) = L_{nl}(r_i)\, Y_{l m_l}(\theta,\phi) \times e^{-\beta r_i}$$

$$-\cancel{\frac{1}{r}}\frac{d}{dr}\phi - \cancel{\frac{Z}{r}}\phi + \dots$$

$$\lim_{r \to 0}$$

$$-\frac{d}{dr}\phi = +Z\phi \quad \to \quad \phi = Ce^{-Zr}$$

1

1

3d

3s 3p

2p ^{6}

α_5 -- α_{10}

2s

2

α_3 α_4

2

α_1 α_2

1s

$n = 1$ $l = 0$

$m_l = 0$

$$\hat{\mathcal{H}} = \hat{\mathcal{H}_0} + \hat{\mathcal{H}_I}$$

$$\hat{\mathcal{H}}_I = \sum_{i<j}^{N} v(x_i, x_j)$$

$$v(x_i, x_j) = v(x_j, x_i)$$

$$v(x_i, x_j) \rightarrow v(|\vec{r}_i - \vec{r}_j|)$$

$$|\vec{r}_i - \vec{r}_j| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

$$v(|\vec{r}_i - \vec{r}_j|) = v(|\vec{r}_j - \vec{r}_i|)$$

$$\Phi_0(x_1, x_2)$$

$$\mathcal{H}_0 \Phi_0(x_1 x_2) = E_0 \Phi_0(x_1 x_2)$$

$$E_0 = \sum_{i=1}^{N=2} \varepsilon_{\alpha_i} = \varepsilon_{\alpha_1} + \varepsilon_{\alpha_2}$$

$$\hat{h}_0(x_i)\, \varphi_{\alpha_i}(x_i) = \varepsilon_{\alpha_i}\, \varphi_{\alpha_i}(x_i)$$

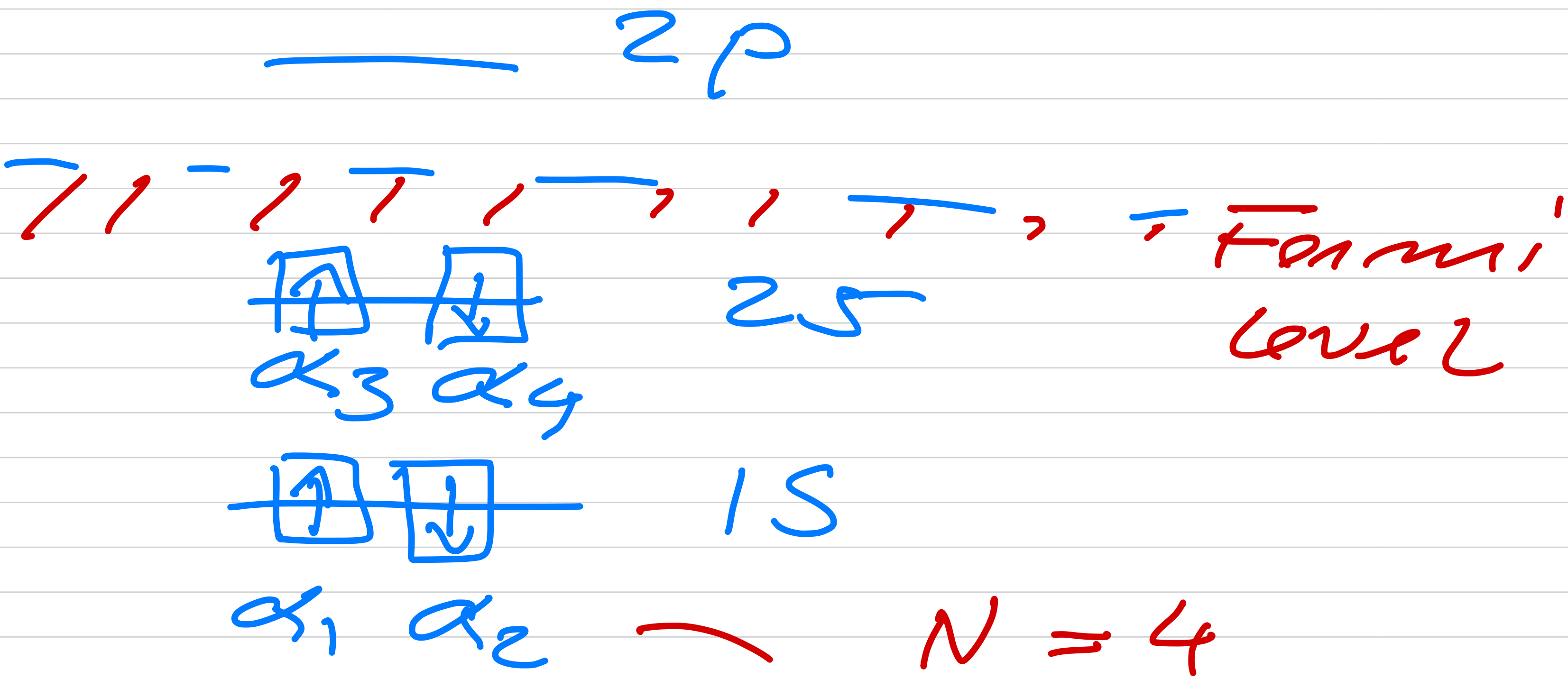
$$\mathcal{H}\, \Phi_0(x_1 x_2) \neq E_0\, \Phi_0(x_1 x_2)$$

$$\underline{\Phi}_0(x_1 x_2) = \frac{1}{\sqrt{2}}\Big(\varphi_{\alpha_1}(x_1)\,\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\,\varphi_{\alpha_2}(x_1)\Big)$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_1}(x_2) \\ \varphi_{\alpha_2}(x_1) & \varphi_{\alpha_2}(x_2) \end{vmatrix}$$

Slater determinant

Atomic Beryllium



$N = 4$

$n = \#$ single-particle states

$\#$ states

$$= \binom{n}{N} = \frac{n!}{(n-N)!\,N!} \qquad n \geq N$$

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle =$$

$$\int dx_1 \int dx_2 \; \Phi_0^*(x_1, x_2) \, H_0 \, \Phi_0(x_1, x_2)$$

$$\langle \Phi_0 | \Phi_0 \rangle = \int dx_1 \int dx_2 \; \Phi_0^* \Phi_0$$

$$= 1$$

(Exercise)

$$\int dx = \sum_{\sigma} \int d\vec{r} \qquad x = (\vec{r}, \sigma)$$

$$= \frac{1}{2}\int dx_1 \int dx_2 \, \overline{\Big[\varphi^*_{\alpha_1}(x_1)\,\varphi^*_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\,\varphi_{\alpha_2}(x_1)\Big]}$$

$$\times \left(\hat{h}_0(x_1) + \hat{h}_0(x_2)\right) \overline{\Big[\varphi_{\alpha_1}(x_1)\,\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\,\varphi_{\alpha_2}(x_1)\Big]}$$

$$= \frac{1}{2}\int dx_1 \int dx_2 \; \varphi^*_{\alpha_1}(x_1)\,\varphi_{\alpha_2}(x_2)\left(\hat{h}_0(x_1) + \hat{h}_0(x_2)\right)\varphi_{\alpha_1}(x_1)\,\varphi_{\alpha_2}(x_2)$$

$$\int dx_1\, \varphi^*_{\alpha_1}(x_1)\, \underbrace{h_0(x_1)\, \varphi_{\alpha_1}(x_1)}_{\varepsilon_{\alpha_1} \varphi_{\alpha_1}(x_1)}$$

$$\times \underbrace{\int dx_2\, \varphi^*_{\alpha_2}(x_2)\, \varphi_{\alpha_2}(x_2)}_{1} \quad = \varepsilon_{\alpha_1}$$

$\varphi_{\alpha_i}(x_j)$ is an ONB

$$\langle \alpha_i | \alpha_j \rangle = \int dx\, \varphi^*_{\alpha_i}(x)\, \varphi_{\alpha_j}(x)$$

$$\underbrace{\int dx_1\, \varphi^*_{\alpha_1}(x_1)\, \varphi_{\alpha_1}(x_1)}_{=1} \int dx_2\, \varphi^*_{\alpha_2}\, \underbrace{h_0(x_2)\, \varphi_{\alpha_2}}_{\varepsilon_{\alpha_2}}$$

cross-term

$$-\frac{1}{2}\int dx_1 \int dx_2 \; \varphi^*_{\alpha_1}(x_1)\,\varphi^*_{\alpha_2}(x_2)$$

$$\times\left(\hat{h}_0(x_1)+\hat{h}_0(x_2)\right)\varphi_{\alpha_1}(x_2)\,\varphi_{\alpha_2}(x_1)$$

$$-\frac{1}{2}\int dx_1\, \varphi^*_{\alpha_1}(x_1)\,\underline{h_0(x_1)}\,\underbrace{\varphi_{\alpha_2}(x_1)}_{\varepsilon_{\alpha_2}\varphi_{\alpha_2}(x_1)} = 0$$

$$\times\int dx_2\, \varphi^*_{\alpha_2}(x_2)\,\varphi_{\alpha_1}(x_2) = 0$$

$$\boxed{\alpha_2 \neq \alpha_1}$$

$$\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle =$$

$$\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2}$$

with N particles

$$\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle = \sum_{i=1}^{N} \varepsilon_{\alpha_i}$$

$$x \in (-\infty, \infty)$$

$$y \in (-\infty, \infty)$$

$$\langle \varphi_{\alpha_i} | \hat{h}_0 | \varphi_{\alpha_i'} \rangle$$

$$= \int dx\, \varphi_{\alpha_i}^*(x)\, \hat{h}_0\, \varphi_{\alpha_i'}(x)$$

$$= \langle \alpha_i | \hat{h}_0 | \alpha_i' \rangle$$

$$\left(\langle i | \hat{h}_0 | i' \rangle \right)$$

$$\langle \Phi_0 | \mathcal{H}_I | \Phi_0 \rangle$$

$$=$$

$$= \int dx_1 \int dx_2 \; \frac{1}{2} \Big[\varphi_{\alpha_1}^*(x_1)\, \varphi_{\alpha_2}^*(x_2) - \varphi_{\alpha_1}^*(x_2)\, \varphi_{\alpha_2}^*(x_1) \Big]$$

$$\times \; v(x_1, x_2) \Big[\varphi_{\alpha_1}(x_1)\, \varphi_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\, \varphi_{\alpha_2}(x_1) \Big]$$

$$\underbrace{\frac{1}{2} \int dx_1 \int dx_2 \; \varphi_{\alpha_1}^*(x_1)\, \varphi_{\alpha_2}^*(x_2)\, v(x_1, x_2)\, \varphi_{\alpha_1}(x_1)\, \varphi_{\alpha_2}(x_2)}_{\langle \alpha_1 \alpha_2 | v | \alpha_1 \alpha_2 \rangle}$$

$$+ \frac{1}{2} \int dx_1 \int dx_2 \; \varphi_{\alpha_1}^*(x_2)\, \varphi_{\alpha_2}^*(x_1)\, \underbrace{v(x_1 x_2)}_{x_1 \Longleftrightarrow x_2} \overset{v(x_2 x_1)}{} \varphi_{\alpha_1}(x_2)\, \varphi_{\alpha_2}(x_1)$$

$$\langle \alpha_1 \alpha_2 | v | \alpha_1 \alpha_2 \rangle$$ — Direct term

$$\langle \alpha_1 \alpha_2 | v | \alpha_2 \alpha_1 \rangle$$ Exchange

$$\int dx_1 \int dx_2 \, \varphi^*_{\alpha_1}(x_1) \, \varphi^*_{\alpha_2}(x_2) \, v(x_1, x_2)$$

$$\times \, \varphi_{\alpha_1}(x_2) \, \varphi_{\alpha_2}(x_1)$$

$$\langle \Phi_c | \hat{H} | \Phi_c \rangle$$

$$= \sum_{i=1}^{N=2} \varepsilon_{\alpha_i}' + \Big(\langle \alpha_1 \alpha_2 | v | \alpha_1 \alpha_2 \rangle$$

$$- \langle \alpha_1 \alpha_2 | v | \alpha_2 \alpha_1 \rangle \Big)$$

$$\langle \underbrace{\alpha_1 \alpha_2}_{I} | v | \underbrace{\alpha_1 \alpha_2}_{J} \rangle_{AS}$$

$$V_{IJ}$$

$$\langle \alpha_i \alpha_j | v | \alpha_k \alpha_\ell \rangle_{AS}$$

$$\rightarrow \langle ij | v | k\ell \rangle_{AS} \quad \begin{matrix} i \leq j \\ k \leq \ell \end{matrix}$$

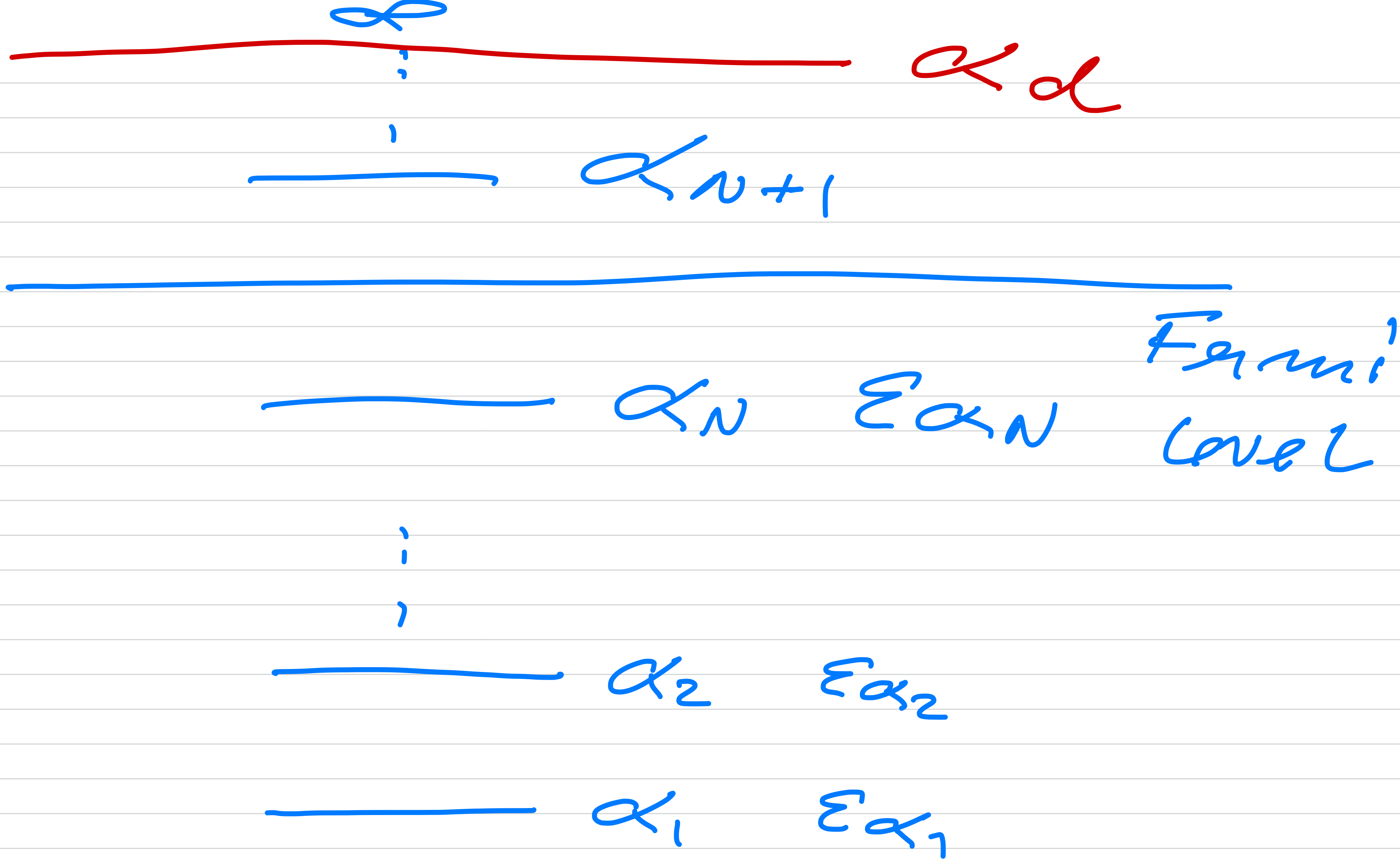
$$= - \langle ji | v | k\ell \rangle_{AS}$$

$$= - \langle ij | v | \ell k \rangle_{AS}$$

$$= \langle ji | v | \ell k \rangle_{AS}$$

$$\Phi_0(x_1\, x_2, \ldots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \cdots & \varphi_{\alpha_1}(x_N) \\ \vdots & & \vdots \\ \varphi_{\alpha_N}(x_1) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

$$\boxed{\alpha_1}\boxed{\alpha_2} \cdots \boxed{\alpha_N} \;\Big|\; \boxed{\alpha_{N+1}} \cdots \boxed{\alpha_d} \;\Big|\; \cdots \infty$$



$$\varepsilon_{\alpha_1} < \varepsilon_{\alpha_2} < \varepsilon_{\alpha_3} \cdots$$

Leibniz representation

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = \boxed{a_{11} a_{22}} - \underset{\substack{P_{12} \\ 1 \leftrightarrow 2}}{a_{21} a_{12}}$$

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

$$= a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} \vdots \\ \vdots \end{vmatrix}$$

$$\overset{(123)}{\boxed{a_{11} a_{22} a_{33}}} - \overset{(132)}{a_{11} a_{23} a_{32}}$$

Leibniz:

$$\det(A) = \sum_{p \in S_n} \operatorname{sgn}(p) \prod_i a_{(pi)i}$$

$$a_{11} a_{22} - a_{12} a_{21}$$