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① Determinant

(why do we talk about determinants? Because it is the simplest basis function for a many-electron wave function!)

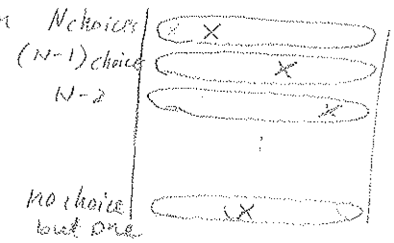
$\mathbb{A}$ is a square $(N\times N)$ matrix

$$\det(\mathbb{A}) = |\mathbb{A}| = \begin{array}{c|ccc|} & \text{clms} & & N \\ \text{rows } 1 & A_{11} & \cdots & A_{1N} \\ \vdots & \vdots & & \vdots \\ N & A_{N1} & \cdots & A_{NN} \end{array} = \sum_{i=1}^{N!} (-1)^{p_i} P_i\, A_{1(1)} A_{2(2)} \cdots A_{N(N)}$$

p_i: # transpositions; (1), (2), …, (N): column indexes; P_i: permutes column indexes

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{1(2)}A_{2(1)}$$

$(-1)^1$ one transposition



choose one from each column, no overlap.

spinorbitals

spatial + spin coordinates of electron 1

$$\Psi(\mathbb{x}_1, \mathbb{x}_2, \cdots, \mathbb{x}_N) \simeq \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbb{x}_1) & \cdots & \phi_1(\mathbb{x}_N) \\ \vdots & & \vdots \\ \phi_N(\mathbb{x}_1) & \cdots & \phi_N(\mathbb{x}_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{p_i} P_i\, \phi_1(\mathbb{x}_1) \cdots \phi_N(\mathbb{x}_N)$$

P_i: permute electrons

— satisfies Pauli anti-symmetry condition

— normalized if $\langle \phi_i(\mathbb{x}_n) | \phi_j(\mathbb{x}_n) \rangle = \delta_{ij}$

$= |\phi_1 \phi_2 \cdots \phi_N\rangle$

short-hand notation

② Properties of determinants

i) $\begin{vmatrix} \cdots & 0 & \cdots \\ & 0 & \\ & \vdots & \\ & 0 & \end{vmatrix} = \begin{vmatrix} & \vdots & \\ 0 & 0 \cdots & 0 \\ & \vdots & \end{vmatrix} = 0$ (one of the electrons does not exist; the whole wave function is zero)

zero clm   zero row

ii) interchange of columns/rows

$$\begin{vmatrix} \cdots & x & \cdots & y & \cdots \end{vmatrix} = (-1) \begin{vmatrix} \cdots & y & \cdots & x & \cdots \end{vmatrix}$$

(Pauli antisymmetry)

iii) $|\mathbb{A}| = |\mathbb{A}^{\dagger}|^*$ adjoint

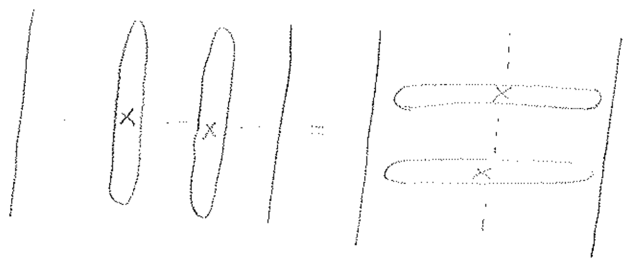
iv) linear combination

$$\begin{vmatrix} A_{11} & \cdots & \sum_k c_k B_{1n}^{(k)} & \cdots & A_{1N} \\ \vdots & & \vdots & & \vdots \\ A_{N1} & \cdots & \sum_k c_k B_{Nn}^{(k)} & \cdots & A_{NN} \end{vmatrix} = \sum_k c_k \begin{vmatrix} A_{11} & \cdots & B_{1n}^{(k)} & \cdots & A_{1N} \\ \vdots & & \vdots & & \vdots \\ A_{N1} & \cdots & B_{Nn}^{(k)} & \cdots & A_{NN} \end{vmatrix}$$

(principle of superposition)

same for row

v) same columns, rows



$= 0$ (Violation of Pauli antisymmetry) or Pauli exclusion

(see ii)

vi) product of matrices

$$|\mathbb{A}\mathbb{B}| = |\mathbb{A}||\mathbb{B}|$$

proof ?

(size-extensivity)

v) $|\mathbb{A}^{-1}| = |\mathbb{A}|^{-1}$ $\left(|\mathbb{E}| = \prod_i e_i \right)$ diagonal matrix ..., inverse does not exist when $|\mathbb{A}| = 0$

vii) unitary transformation

$$|\mathbb{U}^\dagger \mathbb{A} \mathbb{U}| = |\mathbb{U}^\dagger||\mathbb{U}||\mathbb{A}| = |\underbrace{\mathbb{U}^\dagger \mathbb{U}}_{=\mathbb{1}}||\mathbb{A}| = |\mathbb{A}|$$

(orbital invariance of HF theory)

Proof of $|AB| = |A||B|$

$\mathbb{A}$ can be brought to upper triangular form by elementary row operations

① row switch

$$\begin{pmatrix} X \\ Y \end{pmatrix} \longrightarrow \begin{pmatrix} Y \\ X \end{pmatrix} \qquad T = \begin{pmatrix} 1 & & & & \\ & \ddots & & & \\ & & 0 & \cdots & 1 \\ & & \vdots & & \vdots \\ & & 1 & \cdots & 0 \\ & & & & & \ddots \\ & & & & & & 1 \end{pmatrix}$$

② row multiply

$$\begin{pmatrix} X \end{pmatrix} \longrightarrow \begin{pmatrix} mX \end{pmatrix} \qquad T = \begin{pmatrix} 1 & & & \\ & \ddots & & \\ & & m & \\ & & & \ddots \\ & & & & 1 \end{pmatrix}$$

③ row add

$$\begin{pmatrix} X \\ Y \end{pmatrix} \longrightarrow \begin{pmatrix} X+mY \\ Y \end{pmatrix} \qquad T = \begin{pmatrix} 1 & & & & \\ & \ddots & & & \\ & & 1 & \cdots & m \\ & & & \ddots & \vdots \\ & & & & 1 \\ & & & & & \ddots \\ & & & & & & 1 \end{pmatrix}$$

The effect of ①, ②, ③ on determinant is ① multiplies (-1), ② multiplies m ③ no effect. (see iV)

Using ①, $\mathbb{A}$ can be rearranged so that all diagonal elements are nonzero.
Using ③, one can perform Gaussian $\underbrace{\text{elimination}}_{\text{up and down}}$ to bring $\mathbb{A}$ to a diagonal form

$\begin{vmatrix} a_{11} & & 0 \\ & \ddots & \\ 0 & & a_{nn} \end{vmatrix} = \prod_i a_{ii}$. so, $|\mathbb{A}| = \prod_i |\mathbb{E}_i| \prod_i a_{ii}$, where $\underset{\text{diagonal}}{\boxed{\diagdown}} = \prod_i \mathbb{E}_i \mathbb{A}$ and

$\mathbb{E}_i$ is an elementary row op. $|\mathbb{E}_i|$ is the effect of $\mathbb{E}$ on determinant.

One can easily reverse the operation $\mathbb{A} = \prod_i \mathbb{E}_i' \boxed{\diagdown}$.

$$|\mathbb{A}\mathbb{B}| = \left|\prod_i \mathbb{E}_i' \boxed{\diagdown}\, \mathbb{B}\right| = \prod_i |\mathbb{E}_i'|\, |\boxed{\diagdown}|\, |\mathbb{B}| = |\mathbb{A}||\mathbb{B}|$$

③ Dirac braket notation

$$|a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \overset{\text{or}}{=} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_\infty \end{pmatrix} \overset{\text{or}}{=} \psi_a(x) \cdots$$

N-vector $\quad$ ∞-vector $\quad$ function

$$\langle b|a\rangle = (b_1^* b_2^* \cdots)\begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = \sum_i b_i^* a_i \quad \text{inner product}$$

$$= \langle a|b\rangle^*$$

$$\overset{\text{or}}{=} \int \psi_b^*(x)\, \psi_a(x)\, dx$$

i) orthonormality

$$\langle i|j\rangle = \delta_{ij} \quad \text{------} \quad \text{Kronecker's delta } \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases}$$

$$\sum_j \delta_{ij} c_j = c_i$$

↳ δ removes Σ and summation index $j \to i$

ii) completeness

$$|a\rangle = \sum_i c_i |i\rangle \longrightarrow \langle j|a\rangle = \sum_i c_i \underbrace{\langle j|i\rangle}_{\delta_{ji}} = c_j$$

$$= \sum_i |i\rangle\langle i|a\rangle$$

$$= \Big\{\sum_i |i\rangle\langle i|\Big\} |a\rangle$$ for any $|a\rangle$ (that satisfies the same boundary conditions as $\{|i\rangle\}$)

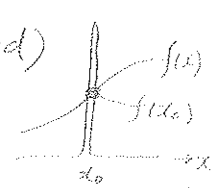
$$\sum_i |i\rangle\langle i| = 1$$ (RI = the resolution of the identity or completeness)

Dirac's delta $\delta(x-x_0) = \begin{cases} \infty, & x = x_0 \\ 0, & x \neq x_0 \end{cases}$

$$\int \delta(x-x_0)\, dx = 1 \quad \text{(normalized)}$$

$$\int \delta(x-x_0)\, f(x)\, dx = f(x_0)$$

↳ δ removes ∫ and integ. variable $x \to x_0$



iii) Operator

$$\hat{O}|a\rangle = |b\rangle \quad \overset{\text{adjoint}}{\Longleftrightarrow} \quad \langle a|\hat{O}^\dagger = \langle b|$$

$$\langle c|\hat{O}|a\rangle = \langle c|b\rangle \qquad \langle a|\hat{O}^\dagger|c\rangle = \langle b|c\rangle = \langle c|b\rangle^*$$

$$\langle a|\hat{O}^\dagger|c\rangle = \langle c|\hat{O}|a\rangle^* \quad (\text{definition of } \hat{O}^\dagger)$$

Hermitian : $\hat{O}^\dagger = \hat{O}$, thus $\langle a|\hat{O}|c\rangle = \langle c|\hat{O}|a\rangle^*$

$$\langle a|\hat{O}|a\rangle = \langle a|\hat{O}|a\rangle^* = \text{real}$$

$$\int \psi_a^* \hat{\Omega} \psi_c \, dx = \int \psi_c^* \Omega^* \psi_a \, dx$$

$\hat{\Omega} = -\frac{\hbar^2}{2m}\nabla^2$, $-i\hbar\frac{\partial}{\partial x}$, $\hat{x}$

are Hermitian

proof?

$$\sum_i \hat{O}|i\rangle\underbrace{\langle i|a\rangle}_{a_i} = \sum_j |j\rangle\underbrace{\langle j|b\rangle}_{b_j}$$

$$\sum_i \underbrace{\langle j|\hat{O}|i\rangle}_{O_{ji}} a_i = b_j$$

O_{ji} ← basis representation / matrix element of $\hat{O}$

$$(O^\dagger)_{ac} = (O)_{ca}^*$$

Hermitian $(O)_{ac} = (O)_{ca}^*$

iv) Change of basis

Orthonomal basis I $\langle i|j\rangle = \delta_{ij}$, $\sum_i |i\rangle\langle i| = 1$

" II $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$, $\sum_\alpha |\alpha\rangle\langle\alpha| = 1$

Transfomation

$$|\alpha\rangle = \sum_i |i\rangle \underbrace{\langle i|\alpha\rangle}_{U_{i\alpha}} = \sum_i |i\rangle (\mathbb{U})_{i\alpha}$$

$$|i\rangle = \sum_\alpha |\alpha\rangle \underbrace{\langle\alpha|i\rangle}_{U^*_{i\alpha}} = \sum_\alpha |\alpha\rangle (\mathbb{U}^\dagger)_{\alpha i}$$

Unitarity

$$\delta_{ji} = \langle j|i\rangle = \sum_\alpha \langle j|\alpha\rangle\langle\alpha|i\rangle = \sum_\alpha (\mathbb{U})_{j\alpha} (\mathbb{U}^\dagger)_{\alpha i} = (\mathbb{U}\mathbb{U}^\dagger)_{ji}$$

$$\mathbb{U}\mathbb{U}^\dagger = \mathbb{U}^\dagger\mathbb{U} = \mathbb{1}$$

An orthogonal to another orthogonal basis transformation is unitary ($\mathbb{U}\mathbb{U}^\dagger = \mathbb{1}$)

$$O_{\alpha\beta} = \langle\alpha|\hat{O}|\beta\rangle = \sum_{i,j} \langle\alpha|i\rangle\langle i|\hat{O}|j\rangle\langle j|\beta\rangle = \sum_{i,j} (\mathbb{U}^\dagger)_{\alpha i} O_{ij} (\mathbb{U})_{j\beta}$$

v) Diagonalization

$$O_{\alpha\beta} = \sum_i (\mathbb{U}^\dagger)_{\alpha i}\, \underline{\underline{\omega_i}}\, (\mathbb{U})_{i\beta}$$

eigenvalue

eigenvectors

If you encounter sym. matrix, always diagonalize it. Something nice may happen!

in other words

$O_{ij} = \omega_i \delta_{ij}$ (if $\hat{O}$ is Hermitian ω is real)

cf.) $\hat{H}|i\rangle = E_i|i\rangle$

Why does every $\overbrace{\text{matrix}}^{N\times N}$ have N eigenvalues? $\mathbb{H}\mathbb{C} = \omega\mathbb{C} \rightarrow (\mathbb{H} - \omega\mathbb{1})\mathbb{C} = 0$

there're N complex slns $\leftarrow$ N^{th} order poly of $\omega = 0$ $\leftarrow$ $|\hat{\mathbb{H}} - \omega\mathbb{1}| = 0 \leftarrow (\mathbb{H} - \omega\mathbb{1})$ has no inverse