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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)

A is a square (N x N) matrix

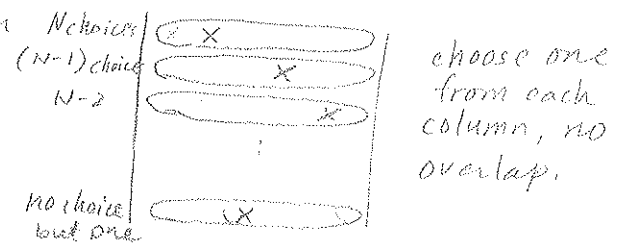
$$\det(A) = |A| = \begin{vmatrix} \text{rows} & \text{cols} & \dots & N \\ 1 & A_{11} & \dots & A_{1N} \\ \vdots & \vdots & \ddots & \vdots \\ N & A_{N1} & \dots & A_{NN} \end{vmatrix}$$

$$= \sum_{\hat{i}=1}^{N!} (-1)^{P_i} P_i A_{1P_1} A_{2P_2} \dots A_{NP_N}$$

transpositions
column indexes
permutes column indexes

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{12}A_{21}$$

one transposition



$$\Psi(x_1, x_2, \dots, x_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \text{spin orbitals} \\ \phi_1(x_1) & \dots & \phi_1(x_N) \\ \vdots & \ddots & \vdots \\ \phi_N(x_1) & \dots & \phi_N(x_N) \end{vmatrix}$$

spatial + spin coordinates of electron i

$$= \frac{1}{\sqrt{N!}} \sum_{\hat{i}=1}^{N!} (-1)^{P_i} P_i \phi_1(x_{P_1}) \dots \phi_N(x_{P_N})$$

permute electrons

- satisfies Pauli anti-symmetry condition
- normalized if $\langle \phi_i(x_n) | \phi_j(x_n) \rangle = \delta_{ij}$

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

short-hand notation

② Properties of determinants

i) $\begin{vmatrix} 0 & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & 0 \end{vmatrix} = \begin{vmatrix} 0 & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & 0 \end{vmatrix} = 0$

zero col / zero row

(one of the electrons does not exist; the whole wave function is zero)

ii) interchange of columns/rows

$$\begin{vmatrix} \dots & x & y & \dots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \dots & y & x & \dots \end{vmatrix} = (-1) \begin{vmatrix} \dots & y & x & \dots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \dots & x & y & \dots \end{vmatrix}$$

(Pauli antisymmetry)

iii) $|A| = |A^\dagger|^*$ adjoint

iv) linear combination

$$\begin{vmatrix} A_{11} & \sum_k c_k B_{1n}^{(k)} & \dots & A_{1N} \\ \vdots & \vdots & \vdots & \vdots \\ A_{N1} & \sum_k c_k B_{Nn}^{(k)} & \dots & A_{NN} \end{vmatrix} = \sum_k c_k \begin{vmatrix} A_{11} & B_{1n}^{(k)} & \dots & A_{1N} \\ \vdots & \vdots & \vdots & \vdots \\ A_{N1} & B_{Nn}^{(k)} & \dots & A_{NN} \end{vmatrix} \quad (\text{principle of superposition})$$

same for row

v) same columns, rows

$$\begin{vmatrix} \vdots & A & \vdots \end{vmatrix} + \begin{vmatrix} \vdots & A & \vdots \end{vmatrix} = \begin{vmatrix} \vdots & A & \vdots \end{vmatrix}$$

$$\begin{vmatrix} \vdots & x & \vdots \\ \vdots & x & \vdots \end{vmatrix} = \begin{vmatrix} \vdots & x & \vdots \\ \vdots & x & \vdots \end{vmatrix} = 0 \quad (\text{Violation of Pauli antisymmetry})$$

(see ii) or Pauli exclusion

vi) product of matrices

$$|A B| = |A| |B| \quad (\text{proof?}) \quad (\text{size-extensivity})$$

v) $|A^{-1}| = |A|^{-1}$ ($|E| = \prod_i \epsilon_i$) \dots , inverse does not exist when $|A| = 0$

↙ diagonal matrix

vii) unitary transformation

$$|U^\dagger A U| = |U^\dagger| |U| |A| = \underbrace{|U^\dagger U|}_{=I} |A| = |A| \quad (\text{orbital invariance of HF theory})$$

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

A can be brought to upper triangular form by elementary row operations

① row switch $\begin{pmatrix} \text{X} \\ \text{Y} \end{pmatrix} \rightarrow \begin{pmatrix} \text{Y} \\ \text{X} \end{pmatrix} \quad T = \begin{pmatrix} 1 & & & \\ & 0 & \dots & 1 \\ & & \ddots & \\ & & & 1 & & \\ & & & & 1 & & \\ & & & & & \ddots & \\ & & & & & & 1 \end{pmatrix}$

② row multiply $\begin{pmatrix} \text{X} \end{pmatrix} \rightarrow \begin{pmatrix} m\text{X} \end{pmatrix} \quad T = \begin{pmatrix} 1 & & & \\ & m & & \\ & & \ddots & \\ & & & 1 \end{pmatrix}$

③ row add $\begin{pmatrix} \text{X} \\ \text{Y} \end{pmatrix} \rightarrow \begin{pmatrix} \text{X} + m\text{Y} \\ \text{Y} \end{pmatrix} \quad T = \begin{pmatrix} 1 & & & \\ & 1 & \dots & m \\ & & \ddots & \\ & & & 1 \end{pmatrix}$

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

Using ①, A can be rearranged so that all diagonal elements are nonzero. Using ③, one can perform Gaussian elimination to bring A to a diagonal form

$$\begin{vmatrix} a_{11} & & 0 \\ & \ddots & \\ 0 & & a_{nn} \end{vmatrix} = \prod_i a_{ii}. \quad \text{So, } |A| = \prod_i |\mathbb{E}_i| \prod_i a_{ii}, \text{ where } \square = \prod_i \mathbb{E}_i A \text{ and diagonal}$$

\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 $A = \prod_i \mathbb{E}'_i \square$.

$$|AB| = \left| \prod_i \mathbb{E}'_i \square B \right| = \prod_i |\mathbb{E}'_i| |\square| |B| = |A||B|$$

③ Dirac bracket notation

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

N-vector ∞ -vector function

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

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

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

i) orthonormality

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

ii) completeness

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

δ removes Σ and summation index $j \rightarrow i$

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

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

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

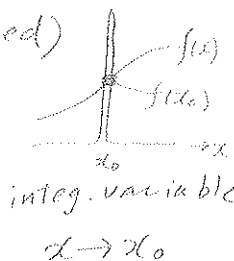
$$\sum_i |i\rangle \langle i| = 1 \quad (\text{RI} = \text{the resolution of the identity or completeness})$$

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

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

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

δ removes \int and



iii) Operator

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

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

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

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

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

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

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 of \hat{O}
matrix element

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

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

iv) Change of basis

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

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

Transformation

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

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

Unitarity

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

$$UU^\dagger = U^\dagger U = 1$$

An orthogonal to another orthogonal basis transformation is unitary ($UU^\dagger = 1$)

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

v) Diagonalization

$$O_{\alpha\beta} = \sum_i (U^\dagger)_{\alpha i} \underbrace{\omega_i}_{\text{eigenvalue}} \underbrace{(U)_{i\beta}}_{\text{eigenvectors}}$$

in other words

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

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

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

Why does every $N \times N$ matrix have N eigenvalues? $H e = \omega e \rightarrow (H - \omega I) e = 0$

there're N complex vals $\leftarrow N^{\text{th}}$ order poly of $\omega=0$ $\leftarrow |H - \omega I| = 0 \leftarrow (H - \omega I)$ has ^{no} inverse