

Solving the Schrödinger Equations of Molecules

Schrödinger equation

$$H\psi = E\psi$$

Free Complement (FC) theory

Pauli principle

$$P\psi = (-)^P \psi$$

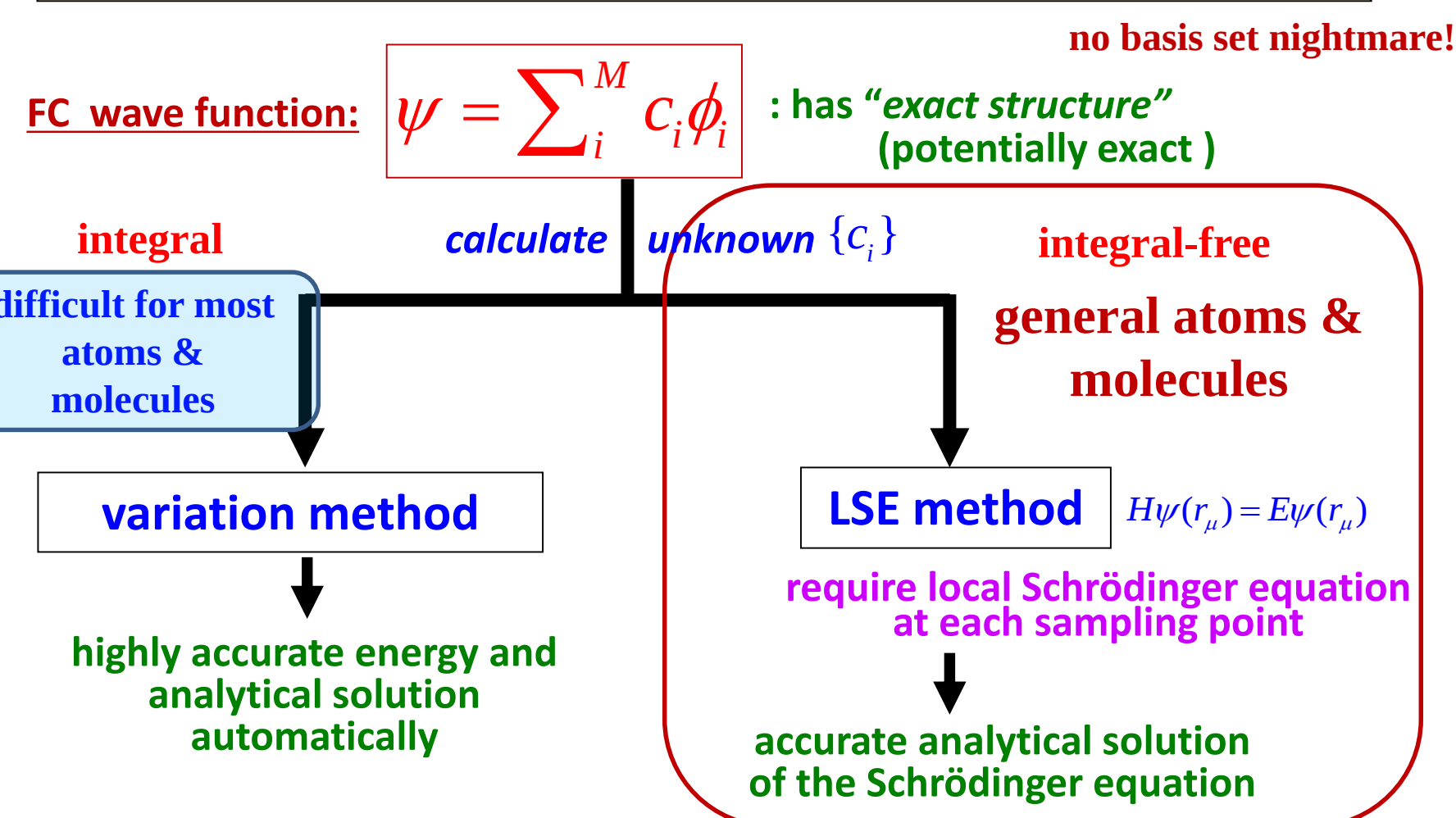
Must be satisfied for electrons
Very time consuming process

Free complement (FC) method for solving the Schrödinger equation

Review: H. Nakatsuji, *Acc. Chem. Res.* 45, 1480 (2012)

H, ψ_0 **FC method** $\rightarrow$ complement function (cf): $\{\phi_i\}$
(complement = element of complete)

Hamiltonian generates its own complete space



FC method of generating complement functions

When we use Slater-type valence-bond (VB) function as ψ_0 , the exact molecular wave function is expressed as

$$\psi = \sum_I c_I \hat{A} \phi_I$$

where the **complement functions (cf's)** ϕ_I is written in **Hartree product form** as

$$\phi_I(1, 2, \dots, N) = \prod_i^{N_e} \left(\exp(-\alpha_i r_{iA}) x_{iA}^{k_{x,iA}} y_{iA}^{k_{y,iA}} z_{iA}^{k_{z,iA}} \left| \vec{r}_{iA} \right|^{k_{r,iA}} \times \prod_{A(\neq B)}^{N_A} r_{iA}^{k_{iA}} \times \prod_{j(>i)}^{N_e} r_{ij}^{m_{ij}} \right) \cdot \sigma_I$$

Pauli principle: Anti-symmetrization

1) Nk algorithm

H. Nakashima, H. Nakatsuji, *J. Chem. Phys.* 139, 044112 (2013).

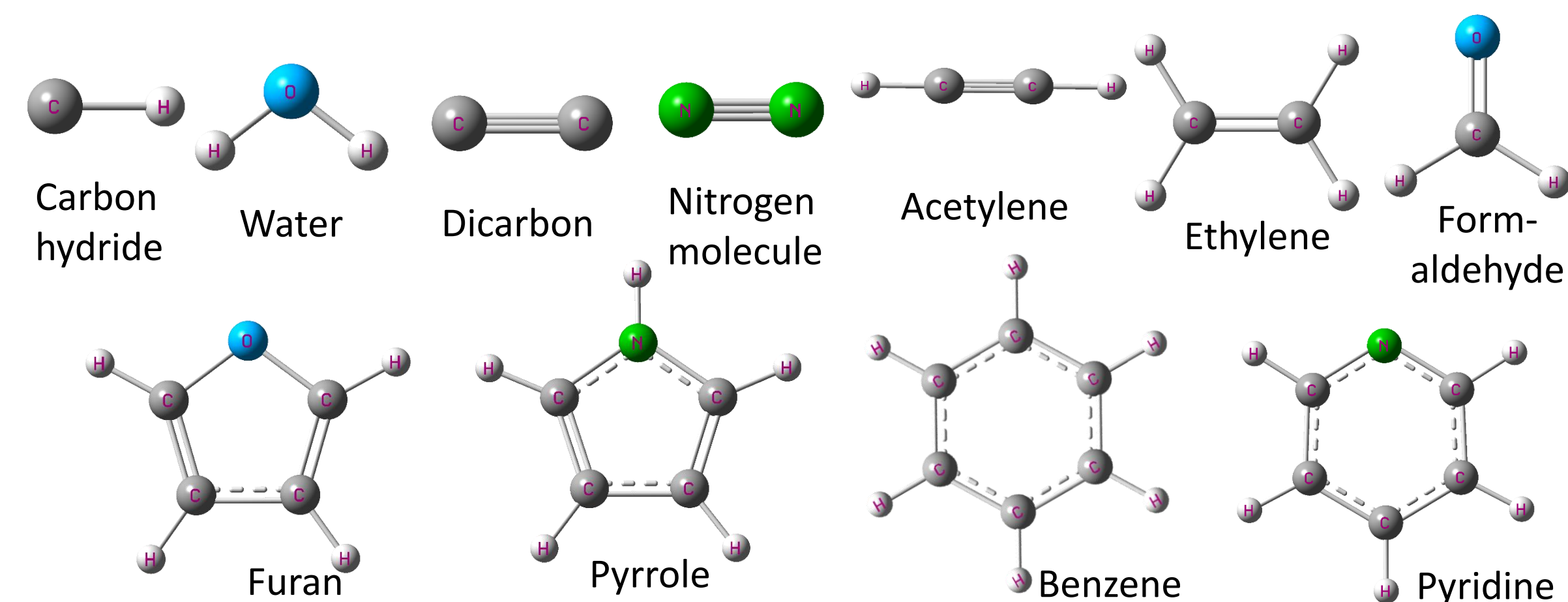
- determinant based **N^{3-4}** algorithm
- not suitable for complex wave functions

2) iExg algorithm

- anti-symmetrization theory for molecules.**
- natural order- N theory.**

These theories would be helpful for doing chemistry in Schrödinger and Dirac accuracy.

Now, organic chemistry can be done in Schrödinger accuracy !!



Order=2

Small organic molecules: ~ 20 electrons

Molecule	No. of Elec.	M_n	Energy (a.u.)		$\Delta E = E_{FC-LSE} - E_{exact}$ (kcal/mol)
			FC-LSE	Exact energy (experiment)	
Carbon Hydride(CH)	7	1503	-38.480 41	-38.479 0	-0.88
Water(H ₂ O)	10	2075	-76.456 78	-76.457 8	0.67
Dicarbon(C ₂)	12	1976	-75.923 69	-75.926 5	-0.44
Dinitrogen(N ₂)	14	1121	-109.542 07	-109.542 7	0.39
Acetylene (C ₂ H ₂)	14	1709	-77.333 31	-77.335 7	1.49
Ethylene (C ₂ H ₄)	16	2628	-78.577 95	-78.587 4	5.93
Formaldehyde (H ₂ CO)	16	4083	-114.505 35	-114.508 0	1.66

The solutions in Schrödinger (Chemical) accuracy could be obtained.

Medium size molecules: ~ 40 electrons

Order=1: test calculation

Molecule	No. of Elec.	M_n	Energy (a.u.)		$\Delta E = E_{FC-LSE} - E_{exact}$ (a.u.)
			FC-LSE	Estimated exact from experiment	
Furan (C ₄ H ₄ O)	36	161	-229.860 1	-230.027	0.167
Pyrrole (C ₄ H ₅ N)	36	174	-209.974 3	-210.173	0.199
Benzene (C ₆ H ₆)	42	398	-232.409 3	-232.248	-0.161
Pyridine (C ₅ H ₅ N)	42	386	-247.704 1	(-248.290)	0.586

Order=2 calculations are necessary for more accurate results.

Parallel algorithm of the FC-LSE method

Step 1. Function generation according to the Hamiltonian

$$\psi_{n+1} = [1 + C_n g(H - E_n)] \psi_n$$

Step 2. FC wave function

$$\psi_{n+1} = \sum_i^{M_n} c_i^{(n)} \phi_i^{(n)}$$

Analytical evaluation
(Small computational cost)

Step 3. LSE equation

Most time consuming step

$$\underline{3.1.} \quad AC = BCE \quad A_{\mu i} = H \phi_i(\mathbf{r}_\mu), \quad B_{\mu i} = \phi_i(\mathbf{r}_\mu)$$

- Distribute sampling points

call MPI_Send($\mathbf{r}_\mu$) call MPI_Recv($\mathbf{r}_\mu$)

- Evaluate $H\phi$ and ϕ at sampling point (10^6 - 10^8 points)

$$\phi(1, 2, \dots, N_e) = A[f_{12}(1, 2) \cdots f_{r-1, r}(r-1, r) \cdot o_1(1) \cdots o_{N_e}(N_e)]$$

Anti-symmetrization: Time consuming

- Even task is distributed to each processor (No communication)

- Peta-flops super parallel machine: Only 1-100 sampling points for single processor

- Cost: $M_n \times N_s \times O(N_e^{3-5})$

M_n : No. of complement functions
 N_s : No. of sampling points
 N_e : No. of electrons

$$\underline{3.2.} \quad HC = SCE \quad H = B^\dagger A, \quad S = B^\dagger B$$

$$H_{ij}^{(Local)} = \sum_\mu^{(Local)} \phi_i(\mathbf{r}_\mu) H \phi_j(\mathbf{r}_\mu)$$

$$S_{ij}^{(Local)} = \sum_\mu^{(Local)} \phi_i(\mathbf{r}_\mu) \phi_j(\mathbf{r}_\mu)$$

- Make local H,S matrices

- Cost: $M_n \times M_n \times N_s$

3.3. Collect H,S matrices and make total H,S matrices

$$H_{ij}^{(All)} = \sum_{n_{proc}} H_{ij}^{(Local)}$$

$$S_{ij}^{(All)} = \sum_{n_{proc}} S_{ij}^{(Local)}$$

- Communication: $M_n \times M_n$

BLAS3 library

call MPI_Reduce(H, MPI_SUM)
call MPI_Reduce(S, MPI_SUM)

Step 4. Diagonalization (Eigenvalue problem)

Use parallelized numerical library

Step 5. Physical observables

$$\text{Energy: } \langle E_L \rangle = \left[\sum_{i,j}^{M_n} C_i C_j H_{ij} \right] / \left[\sum_{i,j}^{M_n} C_i C_j S_{ij} \right] \quad \text{H-square error: } \sigma^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2$$

Small computational cost

Parallel efficiency on TSUBAME2

