

# Wavefunction-based Correlation Methods:

## Basis rotations & Configuration Interaction (CI)

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# Hubbard model

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The Hubbard model proposed in 1963 (named after John Hubbard) is a simple model of interacting particles in a lattice in order to describe the transition between conducting and insulating systems (Mott insulators). Since then, it has been applied to the study of high-temperature superconductivity, quantum magnetism, and charge density waves.

The Fermi-Hubbard Hamiltonian reads

$$\hat{H} = -t \sum_{\langle i,j \rangle} \sum_{\sigma} (a_{i\sigma}^{\dagger} a_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\alpha} n_{i\beta}, \quad (1)$$

where  $a_{i\sigma}^{(\dagger)}$  is the creation (annihilation) operator for  $i$ -th site,  $t$  represents the hopping parameter, and  $U$  represents the on-site Coulomb repulsion.

# Hubbard dimer

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The two-site Hubbard model is a simple example for understanding electron correlation

$$\hat{H} = -t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U(n_{1\alpha} n_{1\beta} + n_{2\alpha} n_{2\beta}). \quad (2)$$

We focus on  $N_e = N_{site} = K/2 = 2$  (half-filling), where the Hilbert space is

$$\mathcal{H}_{N_e=2} = \text{span}\{|1\bar{1}\rangle, |2\bar{2}\rangle, |1\bar{2}\rangle, |2\bar{1}\rangle\} \oplus \text{span}\{|12\rangle\} \oplus \text{span}\{|\bar{1}\bar{2}\rangle\}. \quad (3)$$

By using the second quantization tool, we can find the Hamiltonian matrix (**an exercise!**) in the subspace  $(N_e, M_S) = (2, 0)$  is

$$H = \begin{bmatrix} U & 0 & -t & -t \\ 0 & U & -t & -t \\ -t & -t & 0 & 0 \\ -t & -t & 0 & 0 \end{bmatrix} \quad (4)$$

which can be diagonalized using softwares like MATHEMATICA.

# Spin and spatial symmetry adapted basis

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While the Hamiltonian over Slater determinants are simple to compute, they are not symmetry eigenfunctions. We can easily check  $(\hat{H}, \hat{S}^2, \hat{S}_z, \hat{P}_{12})$  forms a set of mutually commuting operators, where  $\hat{P}_{12}$  is the spatial inversion, which exchanges sites 1 and 2. The group  $\mathcal{G} = \{I, \hat{P}_{12}\}$  is a simple example of **point group**. The advantage of introducing **spin and spatial symmetry adapted basis** [or configuration state functions (CSF)] is that the representation of  $\hat{H}$  will become **block-diagonal**.

# Spin and spatial symmetry adapted basis

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We can introduce the following CSF

$$|\Phi_c^{Sg}\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle + |2\bar{1}\rangle) \quad (5)$$

$$|\Phi_c^{Tu}\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle - |2\bar{1}\rangle) \quad (6)$$

$$|\Phi_i^{Sg}\rangle = \frac{1}{\sqrt{2}}(|1\bar{1}\rangle + |2\bar{2}\rangle) \quad (7)$$

$$|\Phi_i^{Su}\rangle = \frac{1}{\sqrt{2}}(|1\bar{1}\rangle - |2\bar{2}\rangle) \quad (8)$$

where the subscript 'c' ('i') means covalent (ionic), and the superscript 'g' ('u') represents the symmetric/gerade (antisymmetric/ungerade) with respect to  $\hat{P}_{12}$ . Thus, the Hilbert space can be decomposed as

$$\mathcal{H} = \mathcal{H}^{Sg} \oplus \mathcal{H}^{Su} \oplus \mathcal{H}^{Tu}, \quad (9)$$

$$\mathcal{H}^{Sg} = \text{span}\{|\Phi_c^{Sg}\rangle, |\Phi_i^{Sg}\rangle\}, \mathcal{H}^{Su} = \text{span}\{|\Phi_i^{Su}\rangle\}, \mathcal{H}^{Tu} = \text{span}\{|\Phi_c^{Tu}\rangle\}. \quad (10)$$

# Spin and spatial symmetry adapted basis

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The relation between the symmetry-adapted configurations with the original one is

$$(|\Phi_c^{Sg}\rangle, |\Phi_i^{Sg}\rangle, |\Phi_i^{Su}\rangle, |\Phi_c^{Tu}\rangle) = (|1\bar{1}\rangle, |2\bar{2}\rangle, |1\bar{2}\rangle, |2\bar{1}\rangle)W, \quad (11)$$

$$W = \begin{bmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \end{bmatrix} \quad (12)$$

Consequently, the Hamiltonian in this basis  $\tilde{H} = W^\dagger H W$  becomes block-diagonal,

$$\tilde{H} = \tilde{H}^{Sg} \oplus \tilde{H}^{Su} \oplus \tilde{H}^{Tu}, \quad (13)$$

$$\tilde{H}^{Sg} = \begin{bmatrix} 0 & -2t \\ -2t & U \end{bmatrix}, \quad \tilde{H}^{Su} = [U], \quad \tilde{H}^{Tu} = [0]. \quad (14)$$

# Eigenvalues of Hubbard dimer

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The eigenvalue of  $\tilde{H}^{Sg}$  satisfies  $E = xt$

$$x^2 - Ux - 4 = 0, \quad x_{\pm} = \frac{U \pm \sqrt{U^2 + 16}}{2}. \quad (15)$$

The **lowest eigenvalue** is  $x_-(U) = \frac{U - \sqrt{U^2 + 16}}{2}$ , and the unnormalized eigenvector is  $(\frac{1}{4}(U + \sqrt{16 + U^2}), 1)$ . The populations of the covalent and ionic components are

$$p_c(U) = \frac{1}{2}\left(1 + \frac{U}{\sqrt{U^2 + 16}}\right), \quad p_i(U) = \frac{1}{2}\left(1 - \frac{U}{\sqrt{U^2 + 16}}\right). \quad (16)$$

Therefore, the two limiting behaviors are

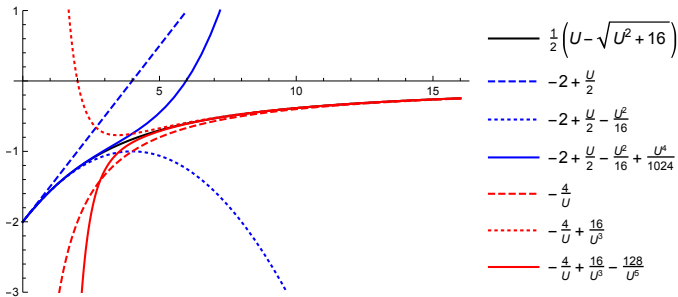
- **Noninteracting limit  $U = 0$ :**  $p_c(U = 0) = p_i(U = 0) = \frac{1}{2}$ ;
- **Strong interaction limit  $U = \infty$ :**  $p_c(U = \infty) = 1$  and  $p_i(U = \infty) = 0$ .



# Eigenvalues of Hubbard dimer

The eigenvalue  $x_-(U) = \frac{U - \sqrt{U^2 + 16}}{2}$  can be expanded around these two limits:

- Small  $U$ :  $x_-(U) \approx -2 + \frac{U}{2}$
- Large  $U$ :  $x_-(U) \approx -\frac{4}{U}$



# Molecular orbital basis

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We can alternatively view the problem from a molecular orbital perspective.

$$(a_g^\dagger, a_u^\dagger) = (a_1^\dagger, a_2^\dagger)C, \quad C = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \quad (17)$$

The configuration written in this basis is related with the previous one by

$$|\Phi_c^{Sg}\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle + |2\bar{1}\rangle) = \frac{1}{\sqrt{2}}(|g\bar{g}\rangle - |u\bar{u}\rangle) \quad (18)$$

$$|\Phi_i^{Sg}\rangle = \frac{1}{\sqrt{2}}(|1\bar{1}\rangle + |2\bar{2}\rangle) = \frac{1}{\sqrt{2}}(|g\bar{g}\rangle + |u\bar{u}\rangle) \quad (19)$$

$$|\Phi_i^{Su}\rangle = \frac{1}{\sqrt{2}}(|1\bar{1}\rangle - |2\bar{2}\rangle) = \frac{1}{\sqrt{2}}(|g\bar{u}\rangle + |u\bar{g}\rangle) \quad (20)$$

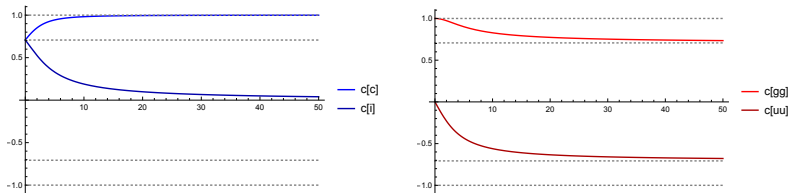
$$|\Phi_c^{Tu}\rangle = \frac{1}{\sqrt{2}}(|1\bar{2}\rangle - |2\bar{1}\rangle) = \frac{1}{\sqrt{2}}(|g\bar{u}\rangle - |u\bar{g}\rangle) \quad (21)$$

# Molecular orbital basis

In the configuration basis  $\{|g\bar{g}\rangle, |u\bar{u}\rangle\}$ , the Hamiltonian reads

$$\tilde{H}^{Sg} = \begin{bmatrix} -2 + \frac{U}{2} & \frac{U}{2} \\ \frac{U}{2} & 2 + \frac{U}{2} \end{bmatrix} \quad (22)$$

Likewise, for the ground state, we can find the coefficients in this basis are



In summary, the two limits are described by

- Noninteracting limit:  $\frac{1}{\sqrt{2}}(|\Phi_c^{Sg}\rangle + |\Phi_i^{Sg}\rangle) = |g\bar{g}\rangle$
- Strong correlation limit:  $|\Phi_c^{Sg}\rangle = \frac{1}{\sqrt{2}}(|g\bar{g}\rangle - |u\bar{u}\rangle)$

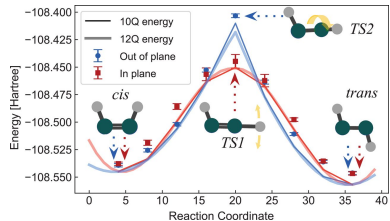
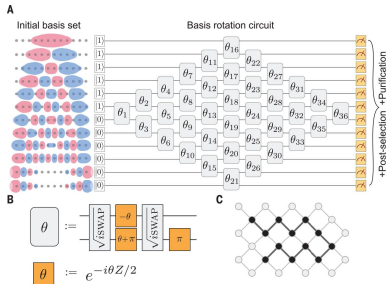
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# Basis rotations

We will show that Hartree-Fock (HF) theory, usually realized by solving the HF equation (stationary condition), can be viewed as an optimization problem, which can be solved by gradually rotating the orbitals to minimize  $E = \langle \Phi(\theta) | \hat{H} | \Phi(\theta) \rangle$ . This view is general and can be generalized to formulate CASSCF.



**Figure 1:** Hartree-Fock on a superconducting qubit quantum computer: Basis rotation circuit[1].

# Basis rotations

Consider a set of spin orbitals  $\{\tilde{\phi}_p\}$  obtained from another set  $\{\phi_q\}$  by a unitary transformation:

$$|\tilde{\phi}_p\rangle = \sum_q |\phi_q\rangle U_{qp} \quad (23)$$

## Exponential parameterization of a unitary matrix

A **unitary** matrix  $\mathbf{U}$  ( $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{I}$ ) can be parameterized as

$$\mathbf{U} = e^{\boldsymbol{\kappa}}, \quad \boldsymbol{\kappa}^\dagger = -\boldsymbol{\kappa}, \quad (24)$$

where  $\boldsymbol{\kappa}$  is an **anti-Hermitian** matrix.

Check (**an exercise**):

$$\mathbf{U}\mathbf{U}^\dagger = e^{\boldsymbol{\kappa}}e^{\boldsymbol{\kappa}^\dagger} = e^{\boldsymbol{\kappa}}e^{-\boldsymbol{\kappa}} = e^{\boldsymbol{\kappa}-\boldsymbol{\kappa}} = \mathbf{I} \quad (25)$$

# Basis rotations

We demonstrate that the following unitary operator performs the orbital rotation.

## Unitary operator for orbital rotations

$$\hat{U}(\boldsymbol{\kappa}) = e^{\hat{\kappa}}, \quad \hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q, \quad (26)$$

$$|\tilde{\phi}_p\rangle = \hat{U}(\boldsymbol{\kappa})|\phi_p\rangle = \sum_q |\phi_q\rangle [e^{\boldsymbol{\kappa}}]_{qp}. \quad (27)$$

Proof: It suffices to show that  $\langle q|e^{-\hat{\kappa}}|p\rangle = [e^{-\boldsymbol{\kappa}}]_{qp}$ . This can be verified term-by-term, e.g.,

$$\langle q|\hat{\kappa}^2|p\rangle = \langle q|\hat{\kappa}\hat{\kappa}|p\rangle = \sum_r \langle q|\hat{\kappa}|r\rangle \kappa_{rp} = \sum_r \kappa_{qr} \kappa_{rp} = [\boldsymbol{\kappa}^2]_{qp}. \quad (28)$$

$$\langle q|\hat{\kappa}^n|p\rangle = \langle q|\hat{\kappa}^{n-1}\hat{\kappa}|p\rangle = \sum_r \langle q|\hat{\kappa}^{n-1}|r\rangle \kappa_{rp} = \sum_r [\boldsymbol{\kappa}^{n-1}]_{qr} \kappa_{rp} = [\boldsymbol{\kappa}^n]_{qp}. \quad (29)$$

# Basis rotations

The advantage of introducing the basis rotation operator  $\hat{U}(\boldsymbol{\kappa})$  is that it can be used to transform not only the single particle states, but also **many-particle basis**. That is,  $\hat{U}(\boldsymbol{\kappa})$  is an operator acting on the Fock space, describing the **induced rotation** by  $\mathbf{U}$  at the single particle level!

## Orbital rotations

$$\begin{aligned} |\tilde{\Phi}\rangle &= \hat{U}(\boldsymbol{\kappa})|\Phi\rangle = \hat{U}(\boldsymbol{\kappa})a_1^\dagger \cdots a_N^\dagger |vac\rangle \\ &= \hat{U}(\boldsymbol{\kappa})a_1^\dagger [\hat{U}^\dagger(\boldsymbol{\kappa})\hat{U}(\boldsymbol{\kappa})] \cdots [\hat{U}^\dagger(\boldsymbol{\kappa})\hat{U}(\boldsymbol{\kappa})]a_N^\dagger [\hat{U}^\dagger(\boldsymbol{\kappa})\hat{U}(\boldsymbol{\kappa})]|vac\rangle \\ &= [\hat{U}(\boldsymbol{\kappa})a_1^\dagger \hat{U}^\dagger(\boldsymbol{\kappa})][\hat{U}(\boldsymbol{\kappa}) \cdots \hat{U}^\dagger(\boldsymbol{\kappa})][\hat{U}(\boldsymbol{\kappa})a_N^\dagger \hat{U}^\dagger(\boldsymbol{\kappa})]\hat{U}(\boldsymbol{\kappa})|vac\rangle \\ &= \tilde{a}_1^\dagger \cdots \tilde{a}_N^\dagger |vac\rangle \end{aligned} \tag{30}$$

where  $\tilde{a}_p^\dagger = \hat{U}(\boldsymbol{\kappa})a_p^\dagger \hat{U}^\dagger(\boldsymbol{\kappa})$ . We will show that  $\tilde{a}_p^\dagger = \sum_q a_q^\dagger U_{qp}$ , which is consistent with the orbital rotation  $|\tilde{\phi}_p\rangle = \sum_q |\phi_q\rangle U_{qp}$ . The mathematical tool is called **Baker-Campbell-Hausdorff (BCH) expansion**.



# Basis rotations

## Baker-Campbell-Hausdorff (BCH) expansion

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!} [A, [A, B]] + \frac{1}{3!} [A, [A, [A, B]]] + \dots \quad (31)$$

Proof: Let  $f(x) = e^{xA} B e^{-xA}$ , the derivative can be evaluated as

$$\frac{df(x)}{dx} = e^{xA} A B e^{-xA} - e^{xA} B A e^{-xA} = e^{xA} [A, B] e^{-xA}, \quad (32)$$

$$\frac{d^2 f(x)}{d^2 x} = e^{xA} [A, [A, B]] e^{-xA}, \quad (33)$$

Using  $f(x) = f(0) + f'(0)x + \frac{1}{2!} f''(0)x^2 + \frac{1}{3!} f'''(0)x^3 + \dots$ , then

$$e^{xA} B e^{-xA} = B + [A, B]x + \frac{1}{2} [A, [A, B]]x^2 + \frac{1}{3!} [A, [A, [A, B]]]x^3 + \dots \quad (34)$$

# Basis rotations

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$$\tilde{a}_p^\dagger = e^{\hat{\kappa}} a_p^\dagger e^{-\hat{\kappa}} = a_p^\dagger + [\hat{\kappa}, a_p^\dagger] + \frac{1}{2!} [\hat{\kappa}, [\hat{\kappa}, a_p^\dagger]] + \frac{1}{3!} [\hat{\kappa}, [\hat{\kappa}, [\hat{\kappa}, a_p^\dagger]]] + \dots \quad (35)$$

The commutators can be evaluated as

$$[\hat{\kappa}, a_p^\dagger] = \sum_{rs} [\kappa_{rs} a_s^r, a_p^\dagger] = \sum_{rs} \kappa_{rs} a_s^r \delta_s^p = \sum_r a^r \kappa_{rp}, \quad (36)$$

$$\begin{aligned} [\hat{\kappa}, [\hat{\kappa}, a_p^\dagger]] &= \sum_r [\hat{\kappa}, a^r] \kappa_{rp} = \sum_r \left( \sum_s a^s \kappa_{sr} \right) \kappa_{rp} \\ &= \sum_s a^s \sum_r \kappa_{sr} \kappa_{rp} = \sum_s a^s [\kappa^2]_{sp} \end{aligned} \quad (37)$$

Thus, indeed  $\tilde{a}_p^\dagger = e^{\hat{\kappa}} a_p^\dagger e^{-\hat{\kappa}}$  corresponds to the creation operator for  $|\tilde{\phi}_p\rangle$ ,

$$\begin{aligned} \tilde{a}_p^\dagger &= a_p^\dagger + \sum_r a_r^\dagger \kappa_{rp} + \frac{1}{2!} \sum_r a_r^\dagger [\kappa^2]_{rp} + \frac{1}{3!} \sum_r a_r^\dagger [\kappa^3]_{rp} + \dots \\ &= \sum_r a_r^\dagger [e^{\kappa}]_{rp} = \sum_r a_r^\dagger U_{rp} \end{aligned} \quad (38)$$

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# HF in terms of orbital rotations

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We have shown that an arbitrary determinant can be parameterized as

$$|\Phi(\boldsymbol{\kappa})\rangle \triangleq \hat{U}(\boldsymbol{\kappa})|\Phi_0\rangle \quad (39)$$

In the Hartree-Fock approximation, the electronic wavefunction is approximated by a single Slater determinant, which is determined by variational optimization of the energy

$$E_{\text{HF}} = \min_{\boldsymbol{\kappa}} E(\boldsymbol{\kappa}), \quad E(\boldsymbol{\kappa}) = \langle \Phi(\boldsymbol{\kappa}) | \hat{H} | \Phi(\boldsymbol{\kappa}) \rangle \quad (40)$$

where the HF energy function can be written as

$$\begin{aligned} E(\boldsymbol{\kappa}) &= \langle \Phi_0 | e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | [\hat{H}, \hat{\kappa}] | \Phi_0 \rangle + \frac{1}{2!} \langle \Phi_0 | [[\hat{H}, \hat{\kappa}], \hat{\kappa}] | \Phi_0 \rangle + \cdots \end{aligned} \quad (41)$$

# HF in terms of orbital rotations

We can set the **current expansion point** to  $\kappa = 0$  by updating  $|\Phi_0\rangle$ . Then, the stationary condition implies that

$$\langle \Phi_0 | [\hat{H}, \delta \hat{\kappa}] | \Phi_0 \rangle = 0 \quad (42)$$

In general, an anti-Hermitian operator  $\hat{\kappa}$  can be written more explicitly as

$$\begin{aligned} \hat{\kappa} &= \sum_{pq} \kappa_{pq} a_p^\dagger a_q = \sum_{p>q} \kappa_{pq} a_p^\dagger a_q + \sum_{p<q} \kappa_{pq} a_p^\dagger a_q + \sum_p \kappa_{pp} a_p^\dagger a_p \\ &= \sum_{p>q} (\kappa_{pq} a_p^\dagger a_q - \kappa_{pq}^* a_q^\dagger a_p) + \sum_p \kappa_{pp} a_p^\dagger a_p \\ &= \sum_{p>q} \kappa_{pq}^R (a_p^\dagger a_q - a_q^\dagger a_p) + \sum_{p>q} i \kappa_{pq}^I (a_p^\dagger a_q + a_q^\dagger a_p) + \sum_p i \kappa_{pp}^I a_p^\dagger a_p \end{aligned} \quad (43)$$

Given  $|\Phi_0\rangle$ , we can partition the orbitals into two sets: **occupied** (occ/closed:  $i, j, k, \dots$ ) and **virtual** (vir:  $a, b, c, \dots$ ).

# HF in terms of orbital rotations

Examine the variations term-by-term:

$$\delta\hat{\kappa} = \sum_{p>q} \delta\kappa_{pq}^R (a_p^\dagger a_q - a_q^\dagger a_p) + \sum_{p>q} i\delta\kappa_{pq}^I (a_p^\dagger a_q + a_q^\dagger a_p) + \sum_p i\delta\kappa_{pp}^I a_p^\dagger a_p \quad (44)$$

- Term 3:  $\langle \Phi_0 | [\hat{H}, a_i^i] | \Phi_0 \rangle = \langle \Phi_0 | [\hat{H}, a_a^a] | \Phi_0 \rangle = 0$ , such that  $\delta\kappa_{pp}$  is redundant, which corresponds to the variation of the phase of each orbital.
- Terms 1 and 2: since  $a_i^j | \Phi_0 \rangle = a_a^b | \Phi_0 \rangle = 0$  for  $i \neq j$  and  $a \neq b$ , then  $\langle \Phi_0 | [\hat{H}, a_i^j \pm a_j^i] | \Phi_0 \rangle = \langle \Phi_0 | [\hat{H}, a_a^b \pm a_b^a] | \Phi_0 \rangle = 0$ . This shows that the occ-occ and vir-vir rotations are redundant, since they do not change  $|\Phi_0\rangle$ . However, occ-vir and vir-occ rotations are nonredundant,

$$\begin{aligned} \langle \Phi_0 | [\hat{H}, a_i^a - a_a^i] | \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} a_i^a | \Phi_0 \rangle + \langle \Phi_0 | a_a^i \hat{H} | \Phi_0 \rangle = f_{ia} + f_{ai} \\ \langle \Phi_0 | [\hat{H}, a_i^a + a_a^i] | \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} a_i^a | \Phi_0 \rangle - \langle \Phi_0 | a_a^i \hat{H} | \Phi_0 \rangle = f_{ia} - f_{ai} \end{aligned}$$

The stationary condition  $\langle \Phi_0 | [\hat{H}, a_i^a - a_a^i] | \Phi_0 \rangle = \langle \Phi_0 | [\hat{H}, a_i^a + a_a^i] | \Phi_0 \rangle = 0$  is equivalent to  $f_{ia} = f_{ai} = 0$  (so-called **Brillouin's theorem**).

# HF in terms of orbital rotations

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Therefore, nonredundant parameterization of  $\hat{\kappa}$  for HF can be written as

$$\hat{\kappa} = \sum_{ai} \kappa_{ai}^R (a_a^\dagger a_i - a_i^\dagger a_a) + \sum_{ai} i \kappa_{ai}^I (a_a^\dagger a_i + a_i^\dagger a_a) \quad (45)$$

This means that the  $\kappa$  matrix has the following structure

$$\kappa = \begin{bmatrix} \mathbf{0}_{CC} & \kappa_{CV} \\ \kappa_{VC} & \mathbf{0}_{VV} \end{bmatrix} = \begin{bmatrix} \mathbf{0}_{CC} & -\kappa_{VC}^\dagger \\ \kappa_{VC} & \mathbf{0}_{VV} \end{bmatrix} \quad (46)$$

The number of nonredundant parameters:  $2n_C n_V$  ( $n_C n_V$ ) for complex (real) HF.

Extensions: For ROHF and CASSCF (discussed later), in which orbitals are partitioned into three sets,  $\kappa$  has the following structure

$$\kappa = \begin{bmatrix} \mathbf{0}_{CC} & \kappa_{CO} & \kappa_{CV} \\ \kappa_{OC} & \mathbf{0}_{OO} & \kappa_{OV} \\ \kappa_{VC} & \kappa_{VO} & \mathbf{0}_{VV} \end{bmatrix} = \begin{bmatrix} \mathbf{0}_{CC} & -\kappa_{OC}^\dagger & -\kappa_{VC}^\dagger \\ \kappa_{OC} & \mathbf{0}_{OO} & -\kappa_{VO}^\dagger \\ \kappa_{VC} & \kappa_{VO} & \mathbf{0}_{VV} \end{bmatrix} \quad (47)$$

# HF in terms of orbital rotations

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Final remark: How is this formulation connected with the usual SCF formulation?

Recall the derivation of HF equation from variational principle

$$\delta L[\{\phi_i\}] = \delta[\langle \Phi_0 | \hat{H} | \Phi_0 \rangle - \sum_{ij} \epsilon_{ji} (\langle \phi_i | \phi_j \rangle - \delta_{ij})] \quad (48)$$

which leads to the HF equation

$$\hat{f}|\phi_i\rangle = \sum_j |\phi_j\rangle \epsilon_{ji} \quad (49)$$

This equation implies that  $f_{ai} = \langle \phi_a | \hat{f} | \phi_i \rangle = \langle \phi_a | \sum_j |\phi_j\rangle \epsilon_{ji} = 0$ . The **canonical HF** equation is obtained by choosing a special set of occupied orbitals, such that  $\epsilon_{ji} = \langle \phi_j | \hat{f} | \phi_i \rangle$  is diagonalized, viz.,  $|\psi_i\rangle = \sum_j |\phi_j\rangle U_{ji}$  and  $\epsilon = \mathbf{U} \epsilon \mathbf{U}^\dagger$ ,

$$\hat{f}|\psi_i\rangle = |\psi_i\rangle \epsilon_i \quad (50)$$



# Full Configuration Interaction (FCI)

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The configuration interaction (CI) is the earliest correlation method. The full CI (FCI) wavefunction can be written as:

$$\begin{aligned} |\Psi_{\text{FCI}}\rangle &= |\Phi_{\text{HF}}\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{i<j,a<b} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots \\ &= (1 + \hat{C}_1 + \hat{C}_2 + \dots) |\Phi_{\text{HF}}\rangle \\ &= (1 + \hat{C}) |\Phi_{\text{HF}}\rangle \end{aligned} \tag{51}$$

which is **the exact method within a given one-electron basis**. The coefficients ( $C_i^a$ ,  $C_{ij}^{ab}$ , etc.) are linear variational parameters. The variational principle leads to a matrix eigenvalue problem

$$\mathbf{H}_{\text{FCI}} \mathbf{C} = E \mathbf{C} \tag{52}$$

# FCI

The FCI Hamiltonian matrix is

$$\mathbf{H}_{\text{FCI}} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} | \Phi_m^d \rangle & \langle \Phi_0 | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_0 | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle & \langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix}$$

The dimension of the matrix is

$$1 + C_N^1 C_{K-N}^1 + C_N^2 C_{K-N}^2 + \dots + C_N^{\min(N, K-N)} C_{K-N}^{\min(N, K-N)} = C_K^N \quad (53)$$

The matrix elements can be evaluated using Slater-Condon rules or second quantization methods discussed before.

# FCI

Using the property that  $\hat{H}$  is **two-body**, as well as the **Brillouin condition**,  $\mathbf{H}_{\text{FCI}}$  based on the HF reference can be simplified to

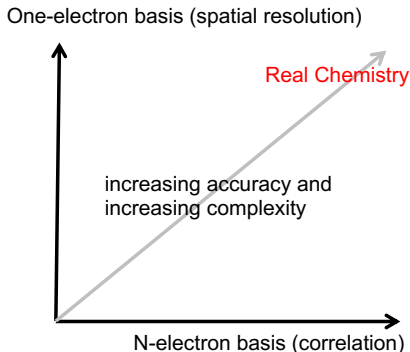
$$\mathbf{H}_{\text{FCI}} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \mathbf{0} & \langle \Phi_0 | \hat{H} | \Phi_{mn}^{de} \rangle & \mathbf{0} & \dots \\ \mathbf{0} & \langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \mathbf{0} & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{mnl}^{def} \rangle & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \quad (54)$$

which is a highly **sparse** matrix with the number nonzero matrix elements per row goes as  $O(N^2(K - N)^2)$ . In comparison, its dimension  $C_K^N$  is **exponential** in the number of electrons  $N$ , as usually  $K \sim O(N)$ .

# Truncated CI

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FCI is only feasible for small systems! Rough estimation on the memory required to store a FCI vector:  $2^{30}$  (8GB),  $2^{40}$  (8TB),  $2^{50}$  (8PB), etc. Therefore, we have to make some approximations in order to treat larger systems.



# Truncated CI

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- **CIS** (configuration interaction singles):

$$\mathbf{H}_{\text{CIS}} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & 0 \\ 0 & \langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle \end{bmatrix} \quad (55)$$

There is no improvement for the ground state if the orbitals are HF orbitals. Diagonalizing the block  $[\langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle]$  gives the simplest method for excited states.

- **CISD** (configuration interaction singles and doubles):

$$\mathbf{H}_{\text{CISD}} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & 0 & \langle \Phi_0 | \hat{H} | \Phi_{mn}^{de} \rangle \\ 0 & \langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mn}^{de} \rangle \\ \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mn}^{de} \rangle \end{bmatrix} \quad (56)$$

This simple method is nowadays replaced by CCSD for several reasons.

# Size-extensivity problem

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Consider  $N$  noninteracting Hubbard dimer/hydrogen molecule in the minimal basis, the Hamiltonian can be written as

$$\hat{H} = \sum_{I=1}^N [\Delta b_I^\dagger b_I + V(b_I^\dagger + b_I)] \quad (57)$$

where  $[b_I, b_J] = 0$  and  $[b_I, b_J^\dagger] = \delta_{IJ}$ . The exact ground state can be written as  $|\Psi\rangle = \prod_{I=1}^N (|0_I\rangle + z|1_I\rangle)$ . The exact can be written as

$$E_N^{\text{FCI}} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{N(1 + z^* z)^{N-1} (\Delta z^* z + V(z^* + z))}{(1 + z^* z)^N} \quad (58)$$

$$= \frac{N(\Delta z^* z + V(z^* + z))}{1 + z^* z} = \textcolor{red}{N} E_{N=1}^{\text{FCI}} \quad (59)$$

This property, called **size-extensivity**, is desirable for correlation methods.

# Size-extensivity problem

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The CISD energy function amounts to keeping terms up to  $z^*z$  in the denominator and numerator in Eq. (58), respectively,

$$E_N^{\text{CISD}} = \frac{N(\Delta z^*z + V(z^* + z))}{(1 + \textcolor{red}{N}z^*z)} \quad (60)$$

The variational condition  $\frac{\partial E_N^{\text{CISD}}}{\partial z^*} = 0$  leads to  $V + \Delta z - NVz^2 = 0$ . In fact,

$$E_N^{\text{FCI}} = \textcolor{red}{N}\frac{1}{2}(\Delta - \sqrt{\Delta^2 + 4V^2}), \quad E_N^{\text{CISD}} = \frac{1}{2}(\Delta - \sqrt{\Delta^2 + 4\textcolor{red}{N}V^2}), \quad (61)$$

which agree with each other only for  $N = 1$ . For large  $N$ ,  $z \sim -1/\sqrt{N}$  and  $E_N^{\text{CISD}} \sim \sqrt{\textcolor{red}{N}}V$ .

This example shows the lack of size-extensivity in CISD. We will introduce CCSD to solve this problem later, but we will not cover methods for approximately restoring size-extensivity (Davidson's correction, CEPA, etc., see Ref. [2]).

# Contents

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- 1 Example for electron correlation: Hubbard dimer
- 2 Basis rotations
- 3 Single-reference theories
  - HF
  - FCI and CISD
- 4 Multi-reference theories
  - CASSCF
  - MRCISD



# CASSCF

Complete-active-space SCF (**CASSCF**) wavefunction Ansatz[2]:

$$|\Psi_{\text{CASSCF}}(\boldsymbol{\kappa}, \mathbf{S})\rangle = e^{\hat{\kappa}} e^{\hat{S}} |\Psi_0\rangle, \quad |\Psi_0\rangle = |\Psi_0^A\rangle |\Phi_0^C\rangle \quad (62)$$

where the orbital and configuration transformations are parameterized as

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q, \quad \boldsymbol{\kappa} = \begin{bmatrix} \mathbf{0}_{\text{CC}} & \boldsymbol{\kappa}_{\text{CO}} & \boldsymbol{\kappa}_{\text{CV}} \\ \boldsymbol{\kappa}_{\text{OC}} & \mathbf{0}_{\text{OO}} & \boldsymbol{\kappa}_{\text{OV}} \\ \boldsymbol{\kappa}_{\text{VC}} & \boldsymbol{\kappa}_{\text{VO}} & \mathbf{0}_{\text{VV}} \end{bmatrix} = \begin{bmatrix} \mathbf{0}_{\text{CC}} & -\boldsymbol{\kappa}_{\text{OC}}^\dagger & -\boldsymbol{\kappa}_{\text{VC}}^\dagger \\ \boldsymbol{\kappa}_{\text{OC}} & \mathbf{0}_{\text{OO}} & -\boldsymbol{\kappa}_{\text{VO}}^\dagger \\ \boldsymbol{\kappa}_{\text{VC}} & \boldsymbol{\kappa}_{\text{VO}} & \mathbf{0}_{\text{VV}} \end{bmatrix} \quad (63)$$

$$\hat{S} = \sum_{n>0} (S_{n0} |n\rangle \langle 0| - S_{0n}^* |0\rangle \langle n|), \quad \mathbf{S} = \begin{bmatrix} 0 & -S_1^* & -S_2^* & \cdots & -S_N^* \\ S_1 & 0 & 0 & \cdots & 0 \\ S_2 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ S_N & 0 & 0 & \cdots & 0 \end{bmatrix} \quad (64)$$

# CASSCF

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The CASSCF energy function is

$$\begin{aligned} E(\boldsymbol{\kappa}, \mathbf{S}) &= \langle \Psi_{\text{CASSCF}}(\boldsymbol{\kappa}, \mathbf{S}) | \hat{H} | \Psi_{\text{CASSCF}}(\boldsymbol{\kappa}, \mathbf{S}) \rangle \\ &= \langle \Psi_0 | e^{-\hat{S}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{S}} | \Psi_0 \rangle \\ &= \langle \Psi_0 | e^{-\hat{S}} (\hat{H} + [\hat{H}, \hat{\kappa}] + \frac{1}{2} [[\hat{H}, \hat{\kappa}], \hat{\kappa}] + \dots) e^{\hat{S}} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | [\hat{H}, \hat{\kappa}] | \Psi_0 \rangle + \langle \Psi_0 | [\hat{H}, \hat{S}] | \Psi_0 \rangle \\ &+ \frac{1}{2} \langle \Psi_0 | [[\hat{H}, \hat{\kappa}], \hat{\kappa}] | \Psi_0 \rangle + \frac{1}{2} \langle \Psi_0 | [[\hat{H}, \hat{S}], \hat{S}] | \Psi_0 \rangle \\ &+ \langle \Psi_0 | [[\hat{H}, \hat{\kappa}], \hat{S}] | \Psi_0 \rangle + \dots \\ &= E_0 + (\mathbf{g}_o^\dagger, \mathbf{g}_c^\dagger) \begin{pmatrix} \mathbf{x}_o \\ \mathbf{x}_c \end{pmatrix} + \frac{1}{2} (\mathbf{g}_o^\dagger, \mathbf{g}_c^\dagger) \begin{pmatrix} \mathbf{H}_{oo} & \mathbf{H}_{oc} \\ \mathbf{H}_{co} & \mathbf{H}_{cc} \end{pmatrix} \begin{pmatrix} \mathbf{x}_o \\ \mathbf{x}_c \end{pmatrix} + \dots (65) \end{aligned}$$

where  $\mathbf{x}_o$  and  $\mathbf{x}_c$  refers to the parameters for orbitals  $\boldsymbol{\kappa}$  and configurations  $\mathbf{S}$ , respectively. This nonlinear function can be optimized by Newton's method introduced before.

# MRCISD

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Uncontracted MRCISD (**uc-MRCISD**): union of single and double excitations from each configuration - the problem is the number of configurations  $\propto O(N_{\text{CAS}})$ .

Internally contraction (**ic-MRCISD**): suppose  $|\Psi_0\rangle$  is the CASSCF reference

- Three classes of singly excited configurations:

$$|\Psi_i^x\rangle, |\Psi_x^a\rangle, |\Psi_i^a\rangle \quad (66)$$

- Eight classes of doubly excited configurations:

$ \Psi_{ij}^{wx}\rangle,  \Psi_{iw}^{xy}\rangle$	internal excitations,
$ \Psi_{ij}^{aw}\rangle,  \Psi_{iw}^{xa}\rangle,  \Psi_{wx}^{ya}\rangle$	semi-internal excitations,
$ \Psi_{ij}^{ab}\rangle,  \Psi_{iw}^{ab}\rangle,  \Psi_{wx}^{ab}\rangle$	double excitations,

(67)

classified by the number of electrons excited in the external space.

# Exercises

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Problem 1: Find the eigenvalues of the following matrix for  $s = +$  and  $s = -$ ,

$$\begin{bmatrix} \Delta + K & K \\ sK & -(\Delta + K) \end{bmatrix}, \quad (68)$$

and discuss when the eigenvalues are not real.

Problem 2: Prove the following identity for Fermionic creation/annihilation operator

$$[a_q^p, a_s^r] = \delta_q^r a_s^p - \delta_s^p a_q^r, \quad a_q^p \triangleq a_p^\dagger a_q \quad (69)$$

Problem 3: If  $\kappa = -\mathbf{i}\theta\sigma_y = \theta \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$  for real  $\theta$ , show that

$$\mathbf{U} = e^\kappa = \begin{bmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix} = \cos(\theta)I_2 - \mathbf{i}\sin(\theta)\sigma_y \quad (70)$$

Problem 4: Let  $|\Phi_0\rangle = |1\bar{1}\rangle$  and a double excitation operator  $\hat{T} = \theta a_2^\dagger a_{\bar{2}}^\dagger a_{\bar{1}} a_1$  for real  $\theta$ , show that

- (i)  $\hat{T}|\Phi_0\rangle = \theta|2\bar{2}\rangle;$
- (ii)  $e^{\hat{T}}|\Phi_0\rangle = |1\bar{1}\rangle + \theta|2\bar{2}\rangle;$
- (iii)  $e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle = \cos(\theta)|1\bar{1}\rangle + \sin(\theta)|2\bar{2}\rangle.$

# Reference I

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- [1] Google AI Quantum et al. “Hartree-Fock on a superconducting qubit quantum computer”. In: *Science* 369.6507 (2020), pp. 1084–1089.
- [2] Peter G Szalay et al. “Multiconfiguration self-consistent field and multireference configuration interaction methods and applications”. In: *Chemical reviews* 112 (2012), pp. 108–181.