- What is convenient is that this second-quantized representation is valid for any number N of electrons:

$$\boxed{\sum_{i=1}^{N} \hat{h}(i) \quad \equiv \quad \sum_{I,J} \langle \varphi_I | \hat{h} | \varphi_J \rangle \hat{a}_I^\dagger \hat{a}_J \quad \equiv \quad \hat{h}}$$

  The information about N has been completely transferred to the states. It does not appear in the operator anymore.

EXERCISE: Let us consider another orthonormal basis $\left\{\tilde{\varphi}_K(X)\right\}_K$ of spin-orbitals that we decompose in the current basis as follows, $|\tilde{\varphi}_P\rangle = \sum_Q U_{QP} |\varphi_Q\rangle$.

(1) Show that the matrix $\mathbf{U}$ is unitary ($\mathbf{U}^\dagger = \mathbf{U}^{-1}$).

(2) Explain why $\hat{a}^\dagger_{\tilde{P}} = \sum_Q U_{QP}\, \hat{a}^\dagger_Q$ and show that $\sum_{I,J} \langle \tilde{\varphi}_I | \hat{h} | \tilde{\varphi}_J \rangle \hat{a}^\dagger_{\tilde{I}} \hat{a}_{\tilde{J}} \equiv \hat{h}$.

Changing the basis in the second-quantized expression of $\hat{h}$.

(1) $\langle\tilde{\varphi}_R|\tilde{\varphi}_P\rangle = \sum_{TQ} U^*_{TR} U_{QP} \underbrace{\langle\varphi_T|\varphi_Q\rangle}_{\delta_{TQ}} = \sum_Q [U^\dagger]_{RQ} U_{QP} = \delta_{RP}$

Since the new basis is also orthonormal

since $|\tilde{\varphi}_R\rangle = \sum_T U_{TR}|\varphi_T\rangle$

Therefore $[U^\dagger U]_{RP} = \delta_{RP} \rightarrow U^\dagger U = [\hat{\mathbb{1}}]$ (identity matrix) $\Rightarrow$ U is unitary.

(2) • $|\tilde{\varphi}_P\rangle = \hat{a}^\dagger_{\tilde{P}}|vac\rangle = \sum_Q U_{QP}\hat{a}^\dagger_Q|vac\rangle \longleftarrow \boxed{\hat{a}^\dagger_{\tilde{P}} = \sum_Q U_{QP}\hat{a}^\dagger_Q}$

• $\sum_{IJ} \langle\tilde{\varphi}_I|\hat{h}|\tilde{\varphi}_J\rangle \hat{a}^\dagger_{\tilde{I}}\hat{a}_{\tilde{J}} = \sum_{IJ}\sum_{TQ} U^*_{TI}U_{QJ}\langle\varphi_T|\hat{h}|\varphi_Q\rangle \hat{a}^\dagger_{\tilde{I}}\hat{a}_{\tilde{J}}$

second-quantized expression in the new basis

$= \sum_{TQ}\langle\varphi_T|\hat{h}|\varphi_Q\rangle \left(\sum_I U^*_{TI}\hat{a}^\dagger_{\tilde{I}}\right)\left(\sum_J U_{QJ}\hat{a}_{\tilde{J}}\right)$

$\sum_{RI} U^*_{TI}U_{RI}\hat{a}^\dagger_R = \sum_R \underbrace{[UU^\dagger]_{RT}}_{\delta_{RT}}\hat{a}^\dagger_R$

$\sum_{JS} U_{QJ}U^*_{SJ}\hat{a}_S = \sum_S \underbrace{[UU^\dagger]_{QS}}_{\delta_{QS}}\hat{a}_S$

Conclusion: $\boxed{\sum_{IJ}\langle\tilde{\varphi}_I|\hat{h}|\tilde{\varphi}_J\rangle \hat{a}^\dagger_{\tilde{I}}\hat{a}_{\tilde{J}} = \hat{h} = \sum_{TQ}\langle\varphi_T|\hat{h}|\varphi_Q\rangle \hat{a}^\dagger_T\hat{a}_Q}$

EX2: By using the relation $e^{-\lambda \hat{A}}\,\hat{B}\,e^{\lambda \hat{A}} = \hat{B} + \int_0^{\lambda} \mathrm{d}\xi\, \frac{\mathrm{d}}{\mathrm{d}\xi}\left(e^{-\xi \hat{A}}\,\hat{B}\,e^{\xi \hat{A}}\right)$, which holds for any λ and any $\hat{B}$ operator, prove the *Baker-Campbell-Hausdorff* (BCH) expansion:

$$e^{-\hat{A}}\,\hat{B}\,e^{\hat{A}} = \hat{B} + \sum_{n=1}^{+\infty} \frac{1}{n!}\,[\![\hat{B},\hat{A}]\!]_n \qquad [\![\hat{B},\hat{A}]\!]_{n+1} = [[\![\hat{B},\hat{A}]\!]_n,\hat{A}], \qquad [\![\hat{B},\hat{A}]\!]_1 = [\hat{B},\hat{A}]$$

$$= \hat{B} + [\hat{B},\hat{A}] + \frac{1}{2}[[\hat{B},\hat{A}],\hat{A}] + \dots$$

BCH expansion

$$\bullet\quad e^{-\lambda\hat{A}}\hat{B}e^{\lambda\hat{A}} = \hat{B} + \int_0^\lambda d\xi\, \underbrace{\frac{d}{d\xi}\left[e^{-\xi\hat{A}}\hat{B}e^{\xi\hat{A}}\right]}_{-e^{-\xi\hat{A}}\hat{A}\hat{B}e^{\xi\hat{A}} + e^{-\xi\hat{A}}\hat{B}\hat{A}e^{\xi\hat{A}}} = \boxed{\hat{B} + \int_0^\lambda d\xi\; e^{-\xi\hat{A}}[\hat{B},\hat{A}]e^{\xi\hat{A}} = e^{-\lambda\hat{A}}\hat{B}e^{\lambda\hat{A}}} \quad (1)$$

$\bullet$ According to (1), $e^{-\xi\hat{A}}[\hat{B},\hat{A}]e^{\xi\hat{A}} = [\hat{B},\hat{A}] + \int_0^\xi d\xi_2\; e^{-\xi_2\hat{A}}[[\hat{B},\hat{A}],\hat{A}]e^{\xi_2\hat{A}}$, thus leading to

replace $\hat{B}$ by $[\hat{B},\hat{A}]$

$$e^{-\lambda\hat{A}}\hat{B}e^{\lambda\hat{A}} = \hat{B} + \int_0^\lambda d\xi\left(\llbracket\hat{B},\hat{A}\rrbracket_1 + \int_0^\xi d\xi_2\; e^{-\xi_2\hat{A}}\llbracket\hat{B},\hat{A}\rrbracket_2 e^{-\xi_2\hat{A}}\right)$$

$$= \hat{B} + \lambda\llbracket\hat{B},\hat{A}\rrbracket_1 + \int_0^\lambda d\xi\int_0^\xi d\xi_2\; \underbrace{e^{-\xi_2\hat{A}}\llbracket\hat{B},\hat{A}\rrbracket_2 e^{-\xi_2\hat{A}}}_{\llbracket\hat{B},\hat{A}\rrbracket_2 + \int_0^{\xi_2} d\xi_3\; e^{-\xi_3\hat{A}}\underbrace{[\llbracket\hat{B},\hat{A}\rrbracket_2,\hat{A}]}_{\llbracket\hat{B},\hat{A}\rrbracket_3}e^{\xi_3\hat{A}}}$$

$$= \hat{B} + \lambda\llbracket\hat{B},\hat{A}\rrbracket_1 + \int_0^\lambda d\xi\int_0^\xi d\xi_2\llbracket\hat{B},\hat{A}\rrbracket_2 + \int_0^\lambda d\xi\int_0^\xi d\xi_2\int_0^{\xi_2} d\xi_3\; \underbrace{e^{-\xi_3\hat{A}}\llbracket\hat{B},\hat{A}\rrbracket_3 e^{-\xi_3\hat{A}}}_{\llbracket\hat{B},\hat{A}\rrbracket_3 + \cdots}$$

by iterating further

$$= \hat{B} + \lambda\llbracket\hat{B},\hat{A}\rrbracket_1 + \sum_{n=2}^{+\infty} \underbrace{\int_0^\lambda d\xi\int_0^\xi d\xi_2\int_0^{\xi_2} d\xi_3 \cdots \int_0^{\xi_{n-1}} d\xi_n\; \llbracket\hat{B},\hat{A}\rrbracket_n}_{}$$

$$\llbracket\hat{B},\hat{A}\rrbracket_n \times \int_0^\lambda d\xi\int_0^\xi d\xi_2\int_0^{\xi_2} d\xi_3 \cdots \underbrace{\int_0^{\xi_{n-2}} d\xi_{n-1}\; \xi_{n-1}}_{\frac{\xi_{n-2}^2}{2}} = \llbracket\hat{B},\hat{A}\rrbracket_n \times \int_0^\lambda d\xi \underbrace{\int_0^\xi d\xi_2\; \frac{\xi_{n-(n-2)}^{n-2}}{(n-2)!}}_{} \qquad \int_0^\lambda \frac{\xi^{n-1}}{(n-1)!}\,d\xi$$

Conclusion: $\boxed{e^{-\lambda\hat{A}}\hat{B}e^{\lambda\hat{A}} = \hat{B} + \sum_{n=1}^{+\infty}\frac{\lambda^n}{n!}\llbracket\hat{B},\hat{A}\rrbracket_n}$ $\rightarrow$ The BCH is obtained for $\lambda = 1$.

EX1: Using **EX2**, show that in second quantization the unitary transformation can be simply written as

$$\hat{a}^\dagger_{\tilde{P}} = \sum_Q \left(e^{-\boldsymbol{\kappa}}\right)_{QP} \hat{a}^\dagger_Q = \boxed{e^{-\hat{\kappa}}\; \hat{a}^\dagger_P \; e^{\hat{\kappa}} = \hat{a}^\dagger_{\tilde{P}}} \qquad \text{where} \qquad \hat{\kappa} = \sum_{PQ} \kappa_{PQ}\; \hat{a}^\dagger_P \hat{a}_Q$$

(EX)

$$\hat{a}^{+}_{\tilde{P}} = e^{-\hat{K}} \hat{a}^{+}_{P} e^{\hat{K}} = \hat{f}(\hat{K})$$

$$|\tilde{P}\rangle = \sum_{Q} \underbrace{U_{QP}}_{(e^{-K})_{QP}} |Q\rangle , \quad \hat{K} = \sum_{PQ} K_{PQ} a^{+}_{P} a_{Q}$$

$$\hat{f}(\hat{K}) = \sum_{n=0}^{+\infty} \frac{1}{n!} [\![\hat{a}^{+}_{P}, \hat{K}]\!]_{n}$$

$$[\![\hat{a}^{+}_{P}, \hat{K}]\!]_{0} = \hat{a}^{+}_{P} = \sum_{Q} \delta_{PQ} \hat{a}^{+}_{Q}$$

$$[\![\hat{a}^{+}_{P}, \hat{K}]\!]_{1} = [\hat{a}^{+}_{P}, \hat{K}]$$

$$= \sum_{RS} K_{RS} [\hat{a}^{+}_{P}, \hat{a}^{+}_{R} \hat{a}_{S}]$$

$$\boxed{\begin{aligned}[\hat{A}, \hat{B}\hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} = \hat{A}\hat{B}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= [\hat{A}, \hat{B}]_{+} \hat{C} - \hat{B} [\hat{A}, \hat{C}]_{+}\end{aligned}}$$

$$[\![\hat{a}^{+}_{P}, \hat{K}]\!]_{1} = \sum_{RS} K_{RS} \Big(- a^{+}_{R} \underbrace{[\hat{a}^{+}_{P}, \hat{a}_{S}]_{+}}_{\delta_{PS}} \Big)$$

$$= - \sum_{R} K_{RP} a^{+}_{R} = - \sum_{Q} K_{QP} \hat{a}^{+}_{Q}$$

• Let us prove that $\quad [\![\hat{a}^{+}_{P}, \hat{K}]\!]_{n} = (-1)^{n} \sum_{Q} (K^{n})_{QP} \hat{a}^{+}_{Q}$

$n = 1$ ok

if true for n then $\quad [\![\hat{a}^{+}_{P}, \hat{K}]\!]_{n+1} = [[\![\hat{a}^{+}_{P}, \hat{K}]\!]_{n}, \hat{K}]$

$$= (-1)^{n} \sum_{Q} (K^{n})_{QP} [\hat{a}^{+}_{Q}, \hat{K}]$$

$$= (-1)^{n} \sum_{Q} (K^{n})_{QP} \sum_{RS} K_{RS} \underbrace{[\hat{a}^{+}_{Q}, \hat{a}^{+}_{R} \hat{a}_{S}]}_{- \hat{a}^{+}_{R} \underbrace{[\hat{a}^{+}_{Q}, \hat{a}_{S}]_{+}}_{\delta_{QS}}}$$

$$= (-1)^{n+1} \sum_{Q,R} (K^{n})_{QP} K_{RQ} \hat{a}^{+}_{R}$$

$$[\![\hat{a}_P^\dagger, \hat{K}]\!]_{n+1} = (-1)^{n+1} \sum_R \sum_Q K_{RQ} (K^n)_{QP} \, \hat{a}_R^\dagger = (-1)^{n+1} \sum_R (K^{n+1})_{RP} \, \hat{a}_R^\dagger$$

$$= (-1)^{n+1} \sum_Q (K^{n+1})_{QP} \, \hat{a}_Q^\dagger \qquad \text{it works!}$$

Conclusion:

$$\hat{f}(\hat{K}) = \sum_{n=0}^{+\infty} \frac{1}{n!} (-1)^n \sum_Q (K^n)_{QP} \, \hat{a}_Q^\dagger$$

$$= \sum_Q \left(\sum_{n=0}^{+\infty} \frac{(-1)^n K^n}{n!} \right)_{QP} \hat{a}_Q^\dagger = \sum_Q \left(e^{-K}\right)_{QP} \hat{a}_Q^\dagger$$

$\boxed{\textbf{EX7:}}$ Show that $E^{\text{o}[1]}_{0,pq} = \langle \Psi^{(0)} | [\hat{E}_{pq} - \hat{E}_{qp}, \hat{H}] | \Psi^{(0)} \rangle$ and $E^{c[1]}_{0} = 2\Big(\mathbf{H}^{\text{CAS}} - E(0)\Big)\mathbf{C}^{(0)}$

where $\mathbf{H}^{\text{CAS}}_{ij} = \langle i | \hat{H} | j \rangle$ and $\mathbf{C}^{(0)} = \begin{bmatrix} \vdots \\ C^{(0)}_i \\ \vdots \end{bmatrix}$

Note: $E^{\text{o}[1]}_{0} = 0$ is known as generalized Brillouin theorem.

$$\frac{\partial}{\partial\delta_i}|\Psi(\lambda)\rangle\Big|_{\lambda=0} = \hat{Q}|i\rangle \rightarrow \quad E^{c[1]}_{0,i} = 2\langle\Psi_0|\hat{H}\,\hat{Q}|i\rangle = 2\left(\langle\Psi_0|\hat{H}|i\rangle - \langle\Psi_0|i\rangle E(0)\right)$$

$$= 2\langle i|(\hat{H} - E(0)\hat{\mathbb{1}}|\Psi_0\rangle$$

$$= 2\sum_j C_j^{(0)}\langle i|\hat{H} - E(0)\hat{\mathbb{1}}|j\rangle$$

$$E^{c[1]}_{0,i} = 2\sum_j C_j^{(0)}\left(H^{CAS}_{ij} - E(0)\delta_{ij}\right)$$

$$\left(H^{CAS}C^{(0)} - E(0)C^{(0)}\right) = E_0^{c[1]}$$

GBT $\quad E^{o[1]}_{0,ai} = \langle\Psi^{(0)}|(E_{ai} - E_{ia})\hat{H}|\Psi^{(0)}\rangle - \langle\Psi^{(0)}|\hat{H}(E_{ai} - E_{ia})|\Psi^{(0)}\rangle$

$$= -\langle\Psi^{(0)}|E_{ia}\hat{H}|\Psi^{(0)}\rangle - \langle\Psi^{(0)}|\hat{H}|E_{ai}|\Psi^{(0)}\rangle$$

$$= -2\langle\Psi^{(0)}|\hat{H}\hat{E}_{ai}|\Psi^{(0)}\rangle = 0$$ for the converged solution.

EXERCISE:

(1) Show that each contribution to the electronic Hamiltonian reads in second quantization as follows,

$$\hat{T} \equiv -\frac{1}{2}\int d\mathbf{r} \sum_{\sigma} \hat{\Psi}^{\dagger}(\mathbf{r},\sigma)\nabla^2_{\mathbf{r}}\hat{\Psi}(\mathbf{r},\sigma), \qquad \hat{V}_{\rm ne} \equiv \int d\mathbf{r}\, v_{\rm ne}(\mathbf{r})\, \hat{n}(\mathbf{r}),$$

$$\hat{W}_{\rm ee} \equiv \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \sum_{\sigma\sigma'} \frac{\hat{\Psi}^{\dagger}(\mathbf{r},\sigma)\hat{\Psi}^{\dagger}(\mathbf{r}',\sigma')\hat{\Psi}(\mathbf{r}',\sigma')\hat{\Psi}(\mathbf{r},\sigma)}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')\hat{n}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}.$$

(2) At the non-relativistic level, real algebra can be used, $\varphi_I(X) = \varphi_{i\sigma}(\mathbf{r},\tau) = \phi_i(\mathbf{r})\delta_{\sigma\tau}$,

$$\hat{h} \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\rm ne}(\mathbf{r})\times \quad \text{and} \quad \hat{w}_{\rm ee} \equiv \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\times \ .$$

Show that the Hamiltonian, that is here a spin-free operator, can be rewritten in the basis of the molecular orbitals $\Big\{\phi_p(\mathbf{r})\Big\}_p$ as follows

$$\boxed{\hat{H} = \sum_{p,q} h_{pq}\hat{E}_{pq} + \frac{1}{2}\sum_{p,q,r,s}\langle pr|qs\rangle\Big(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\Big)}$$

where $\hat{E}_{pq} = \sum_{\sigma} \hat{a}^{\dagger}_{p,\sigma} \hat{a}_{q,\sigma}$, $\quad h_{pq} = \langle \phi_p | \hat{h} | \phi_q \rangle$ and

$$\langle pr|qs\rangle = \int \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \; \phi_p(\mathbf{r}_1)\phi_r(\mathbf{r}_2) \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \phi_q(\mathbf{r}_1)\phi_s(\mathbf{r}_2) = (pq|rs).$$

Hamiltonian in terms of the field operators

- $$\hat{T} \equiv \sum_{IJ} \langle \varphi_I | \hat{t} | \varphi_J \rangle \hat{a}_I^+ \hat{a}_J = \sum_{IJ} \int dx\, \varphi_I^*(x) \times \left(-\frac{1}{2}\nabla_{\vec{r}}^2 \varphi_J(x)\right) \hat{a}_I^+ \hat{a}_J$$

$$= -\frac{1}{2}\int dx \underbrace{\sum_I \varphi_I^*(x)\hat{a}_I^+}_{\hat{\psi}^+(x)} \nabla_{\vec{r}}^2 \underbrace{\left[\sum_J \varphi_J(x)\hat{a}_J\right]}_{\hat{\psi}(x)} = \boxed{-\frac{1}{2}\int d\vec{r} \sum_\sigma \hat{\psi}^+(\vec{r},\sigma)\nabla_{\vec{r}}^2 \hat{\psi}(\vec{r},\sigma) = \hat{T}}$$

- $$\hat{W}_{ee} \equiv \frac{1}{2}\sum_{IJKL} \int dx \int dx'\, \varphi_I^*(x)\varphi_J^*(x') \frac{1}{|\vec{r}-\vec{r}'|} \varphi_K(x)\varphi_L(x')\, \hat{a}_I^+ \hat{a}_J^+ \hat{a}_L \hat{a}_K$$

$$= \frac{1}{2}\int dx \int dx' \frac{1}{|\vec{r}-\vec{r}'|} \underbrace{\left(\sum_I \varphi_I^*(x)\hat{a}_I^+\right)}_{\hat{\psi}^+(x)} \underbrace{\left(\sum_J \varphi_J^*(x')\hat{a}_J^+\right)}_{\hat{\psi}^+(x')} \underbrace{\left(\sum_L \varphi_L(x')\hat{a}_L\right)}_{\hat{\psi}(x')} \underbrace{\left(\sum_K \varphi_K(x)\hat{a}_K\right)}_{\hat{\psi}(x)}$$

$$= \frac{1}{2}\int d\vec{r}\int d\vec{r}' \frac{1}{|\vec{r}-\vec{r}'|} \sum_{\sigma\sigma'} \hat{\psi}^+(\vec{r},\sigma) \underbrace{\hat{\psi}^+(\vec{r}',\sigma')\hat{\psi}(\vec{r}',\sigma')\hat{\psi}(\vec{r},\sigma)}_{-\underbrace{\hat{\psi}^+(\vec{r}',\sigma')\hat{\psi}(\vec{r},\sigma)}_{\downarrow\ \delta_{\sigma\sigma'}\delta(\vec{r}'-\vec{r}) - \hat{\psi}(\vec{r},\sigma)\hat{\psi}^+(\vec{r}',\sigma')}\hat{\psi}(\vec{r}',\sigma')} = \frac{1}{2}\int d\vec{r}\int d\vec{r}' \frac{1}{|\vec{r}-\vec{r}'|}\left(\hat{n}(\vec{r})\hat{n}(\vec{r}') - \delta(\vec{r}-\vec{r}')\hat{n}(\vec{r})\right)$$

- $$\hat{V}_{ne} \equiv \int d\vec{r}\, v_{ne}(\vec{r}) \underbrace{\sum_\sigma \hat{\psi}^+(\vec{r},\sigma)\hat{\psi}(\vec{r},\sigma)}_{\hat{n}(\vec{r})}.$$

(1) $$\hat{H} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^{+} \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_R | \hat{w}_{ee} | \varphi_Q \varphi_S \rangle \hat{a}_P^{+} \hat{a}_R^{+} \hat{a}_S \hat{a}_Q$$

$$= \sum_{p,q,\sigma,\tau} \langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle \hat{a}^{+}_{p,\sigma} \hat{a}_{q,\tau} + \frac{1}{2} \sum_{pqrs} \sum_{\sigma_1\sigma_2\tau_1\tau_2} \langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle \hat{a}^{+}_{p,\sigma_1} \hat{a}^{+}_{r,\sigma_2} \hat{a}_{s,\tau_2} \hat{a}_{q,\tau_1}$$

where $$\langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle = \int dx\, \varphi^{*}_{p\sigma}(x) (\hat{h}\varphi_{q\tau})(x) = \int d\vec{r} \sum_{\mu=\alpha,\beta} \varphi^{*}_{p\sigma}(\vec{r},\mu) (\hat{h}\varphi_{q\tau})(\vec{r},\mu)$$

spin-free

real algebra!

$$= \int d\vec{r} \sum_{\mu=\alpha,\beta} \phi_p(\vec{r})\, \delta_{\mu\sigma}\, (\hat{h}\phi_q)(\vec{r})\, \delta_{\tau\mu}$$

$$\rightarrow \boxed{\langle \varphi_{p\sigma} | \hat{h} | \varphi_{q\tau} \rangle = \delta_{\sigma\tau}\, h_{pq}}$$

and $$\langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle = \int dx_1 \int dx_2\, \varphi^{*}_{p\sigma_1}(x_1) \varphi^{*}_{r\sigma_2}(x_2) \frac{1}{r_{12}} \varphi_{q\tau_1}(x_1) \varphi_{s\tau_2}(x_2)$$ where $r_{12} = |\vec{r}_1 - \vec{r}_2|$

$$= \int d\vec{r}_1 \int d\vec{r}_2 \sum_{\mu=\alpha,\beta} \sum_{\nu=\alpha,\beta} \phi_p(\vec{r}_1)\, \delta_{\sigma_1\mu}\, \phi_r(\vec{r}_2)\, \delta_{\sigma_2\nu} \frac{1}{r_{12}} \phi_q(\vec{r}_1)\, \delta_{\tau_1\mu}\, \phi_s(\vec{r}_2)\, \delta_{\tau_2\nu}$$

$$\boxed{\langle \varphi_{p\sigma_1} \varphi_{r\sigma_2} | \hat{w}_{ee} | \varphi_{q\tau_1} \varphi_{s\tau_2} \rangle = \delta_{\sigma_1\tau_1} \delta_{\sigma_2\tau_2} \langle pr | qs \rangle}$$

Therefore

$$\hat{H} = \sum_{pq\sigma\tau} h_{pq}\,\delta_{\sigma\tau}\,\hat{a}^{\dagger}_{p,\sigma}\hat{a}_{q,\tau} + \frac{1}{2}\sum_{pqrs}\sum_{\sigma_1\sigma_2\tau_1\tau_2}\langle pr|qs\rangle\,\delta_{\sigma_1\tau_1}\delta_{\sigma_2\tau_2}\,\hat{a}^{\dagger}_{p,\sigma_1}\hat{a}^{\dagger}_{r,\sigma_2}\hat{a}_{s,\tau_2}\hat{a}_{q,\tau_1}$$

$$= \sum_{pq} h_{pq}\underbrace{\left(\sum_{\sigma}\hat{a}^{\dagger}_{p,\sigma}\hat{a}_{q,\sigma}\right)}_{\hat{E}_{pq}} + \frac{1}{2}\sum_{pqrs}\langle pr|qs\rangle\sum_{\sigma_1\sigma_2}\underbrace{\hat{a}^{\dagger}_{p,\sigma_1}\hat{a}^{\dagger}_{r,\sigma_2}\hat{a}_{s,\sigma_2}\hat{a}_{q,\sigma_1}}_{-\hat{a}^{\dagger}_{p,\sigma_1}\underbrace{\hat{a}^{\dagger}_{r,\sigma_2}\hat{a}_{q,\sigma_1}}_{\delta_{\sigma_1\sigma_2}\delta_{rq}-\hat{a}_{q,\sigma_1}\hat{a}^{\dagger}_{r,\sigma_2}}\hat{a}_{s,\sigma_2}}$$

$$\rightarrow \boxed{\hat{H} = \sum_{pq} h_{pq}\hat{E}_{pq} + \frac{1}{2}\sum_{pqrs}\langle pr|qs\rangle\left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\right)}$$