

# Foundations of quantum chemistry

## *3. Reduced density matrices*

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# Entangled vs non-entangled states

- A **non-entangled** pure state (slide 1.97):

$$\Psi(1, 2) = \psi(1) \otimes \phi(2) \quad \Rightarrow \quad \langle A(1) \rangle_{\Psi(1,2)} = \langle \psi(1) | \hat{A}(1) | \psi(1) \rangle$$

We can assign an individual **pure** state to 1 (or 2).

- An **entangled** pure state (slide 1.97):

$$\Psi(1, 2) = \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2)$$

$$\langle A(1) \rangle_{\Psi(1,2)} = \sum_j p_j \langle \psi''_j(1) | \hat{A}(1) | \psi''_j(1) \rangle$$

We can't assign an individual **pure** state to 1 (or 2), but we can assign it a **mixed** state. Which is its **density operator**?

# 1-particle expected values

- Let  $\{\dots \psi_i(1) \dots\}$  and  $\{\dots \phi_j(2) \dots\}$  be *orthonormal* basis sets.

$$\begin{aligned}
 \langle A(1) \rangle_\rho &= Tr \left( \hat{A}(1) \hat{\rho}(1, 2) \right) = \sum_{ij} \left\langle \psi_i(1) \phi_j(2) \left| \hat{A}(1) \hat{\rho}(1, 2) \right| \psi_i(1) \phi_j(2) \right\rangle \\
 &= \sum_{ij} \underbrace{\langle \psi_i(1) \phi_j(2) |}_{\text{green}} \underbrace{\hat{A}(1)}_{\text{blue}} \underbrace{\sum_{kl} \langle \psi_k(1) \phi_l(2) |}_{\text{red}} \underbrace{\langle \psi_k(1) \phi_l(2) |}_{\text{green}} \hat{\rho}(1, 2) | \psi_i(1) \phi_j(2) \rangle \\
 &= \sum_{ij} \sum_{kl} \underbrace{\langle \psi_i(1) | \hat{A}(1) | \psi_k(1) \rangle}_{\text{blue}} \underbrace{\langle \phi_j(2) | \phi_l(2) \rangle}_{\text{green}} \langle \psi_k(1) \phi_l(2) | \hat{\rho}(1, 2) | \psi_i(1) \phi_j(2) \rangle \\
 &\quad \text{definition of the matrix representation of } \hat{\rho}_1(1) \rightarrow \langle \psi_k(1) | \hat{\rho}_1(1) | \psi_i(1) \rangle \\
 &= \sum_i \sum_k \langle \psi_i(1) | \hat{A}(1) | \psi_k(1) \rangle \sum_j \langle \psi_k(1) \phi_j(2) | \hat{\rho}(1, 2) | \psi_i(1) \phi_j(2) \rangle \\
 &= \sum_i \langle \psi_i(1) | \hat{A}(1) \hat{\rho}_1(1) | \psi_i(1) \rangle = Tr \left( \hat{A}(1) \hat{\rho}_1(1) \right)
 \end{aligned}$$

# 1-particle or 1<sup>st</sup>-order reduced d. o.

- *Definition:*  $\hat{\rho}_1(1) = \sum_j \langle \phi_j(2) | \hat{\rho}(1, 2) | \phi_j(2) \rangle \equiv Tr_2 \hat{\rho}(1, 2)$

Taking the **partial trace over particle 2** of the density operator can be interpreted as averaging it over the degrees of freedom of particle 2.

- *Matrix representation:*

$$\langle \psi_k(1) | \hat{\rho}_1(1) | \psi_i(1) \rangle = \langle \psi_k(1) | \sum_j \langle \phi_j(2) | \hat{\rho}(1, 2) | \phi_j(2) \rangle | \psi_i(1) \rangle$$

$(m_1, m_1)$        $(m_1 \times m_2, m_1 \times m_2)$

$$\rho_1 = Tr_2 \rho$$

$$= \sum_j \langle \psi_k(1) | \phi_j(2) | \hat{\rho}(1, 2) | \psi_i(1) | \phi_j(2) \rangle$$

- *Example: 2 spin-1/2 particles.*

$$(\rho_1)_{\alpha,\beta} = \rho_{\alpha\alpha,\beta\alpha} + \rho_{\alpha\beta,\beta\beta}$$

$$\rho(1, 2) = \begin{pmatrix} \rho_{\alpha\alpha,\alpha\alpha} & \rho_{\alpha\alpha,\alpha\beta} & \rho_{\alpha\alpha,\beta\alpha} & \rho_{\alpha\alpha,\beta\beta} \\ \rho_{\alpha\beta,\alpha\alpha} & \rho_{\alpha\beta,\alpha\beta} & \rho_{\alpha\beta,\beta\alpha} & \rho_{\alpha\beta,\beta\beta} \\ \rho_{\beta\alpha,\alpha\alpha} & \rho_{\beta\alpha,\alpha\beta} & \rho_{\beta\alpha,\beta\alpha} & \rho_{\beta\alpha,\beta\beta} \\ \rho_{\beta\beta,\alpha\alpha} & \rho_{\beta\beta,\alpha\beta} & \rho_{\beta\beta,\beta\alpha} & \rho_{\beta\beta,\beta\beta} \end{pmatrix}$$

$$\rho_1(1) = Tr_2 \rho(1, 2) = \begin{pmatrix} (\rho_1)_{\alpha,\alpha} & (\rho_1)_{\alpha,\beta} \\ (\rho_1)_{\beta,\alpha} & (\rho_1)_{\beta,\beta} \end{pmatrix}$$

$$(\rho_2)_{\alpha,\beta} = \rho_{\alpha\alpha,\alpha\beta} + \rho_{\beta\alpha,\beta\beta}$$

### *Exercise 3.1*

Show that, for the entangled pure state considered in the slide 3.2 (where  $\{\psi_i(1)\}$  and  $\{\phi_j(2)\}$  are orthonormal), the reduced density operator describing the subsystem 1 is (with the notation of slide

1.97):  $\hat{\rho}_1(1) = \sum_r p_r |\psi_r''(1)\rangle \langle \psi_r''(1)|$

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$$1.97): \hat{\rho}_1(1) = \sum_r p_r |\psi_r''(1)\rangle \langle \psi_r''(1)|$$

**Solution:** let us verify that  $\hat{\rho}_1(1)$  allows to calculate the expected value of any observable of subsystem 1:

$$\begin{aligned} Tr \left( \hat{A}(1) \hat{\rho}_1(1) \right) &= Tr \left( \hat{A}(1) \sum_r p_r |\psi_r''(1)\rangle \langle \psi_r''(1)| \right) \\ &= \sum_r p_r Tr \left( \hat{A}(1) |\psi_r''(1)\rangle \langle \psi_r''(1)| \right) \\ &= \sum_r p_r \langle \psi_r''(1) | \hat{A}(1) \psi_r''(1) \rangle = \langle A(1) \rangle_{\Psi(1,2)} \end{aligned}$$

slide 1.97

- For an ***N*-particle** compound system:

$$\begin{aligned}\hat{\rho}_1(1) &= Tr_{2\dots N} \hat{\rho}(1, 2, \dots, N) \\ &= \sum_{j_2 \dots j_N} \langle \phi_{j_2}(2) \dots \phi_{j_N}(N) | \hat{\rho}(1, 2, \dots, N) | \phi_{j_2}(2) \dots \phi_{j_N}(N) \rangle\end{aligned}$$

## 2-particle or 2<sup>nd</sup>-order reduced d. o.

- If we are interested in properties of particle 1, particle 2 or joint properties of both (e.g., their coulombic repulsion) of an ***N*-particle** system we need the 2-particle (or 2<sup>nd</sup> order) reduced density operator:

$$\begin{aligned}\widehat{\rho}_{1,2}(1, 2) &= Tr_{3\dots N} \hat{\rho}(1, 2, \dots, N) \\ &= \sum_{j_3 \dots j_N} \langle \phi_{j_3}(3) \dots \phi_{j_N}(N) | \hat{\rho}(1, 2, \dots, N) | \phi_{j_3}(3) \dots \phi_{j_N}(N) \rangle\end{aligned}$$

- etc.

### Exercise 3.2

Let us consider a two-particle system in the pure state described by the vector  $\Psi(1, 2) = \psi(1) \otimes \phi(2)$ , where  $\psi(1)$  and  $\phi(2)$  are normalized vectors of the Hilbert spaces of particles 1 and 2 respectively. Show that

$$\hat{\rho}_1(1) = |\psi(1)\rangle \langle \psi(1)|$$

$$\hat{\rho}_2(2) = |\phi(2)\rangle \langle \phi(2)|$$

$$\hat{\rho}(1, 2) = \hat{\rho}_1(1) \otimes \hat{\rho}_2(2)$$

*Hint:* To calculate the partial traces use basis sets containing  $\psi(1)$  or  $\phi(2)$ . To prove the third equation show that its two members give the same result when applied to any basis vector  $\psi_i(1) \otimes \phi_j(2)$  of the compound Hilbert space.

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**Solution:** let us choose basis sets for the Hilbert spaces of subsystems 1 and 2 that contain, as their first element,  $\psi_1(1) = \psi(1)$  and  $\phi_1(2) = \phi(2)$  respectively:

$$\hat{\rho}(1,2) = |\Psi(1,2)\rangle \langle \Psi(1,2)|$$

$$\hat{\rho}_1(1) = \text{Tr}_2 \hat{\rho}(1,2) = \sum_j \underbrace{\langle \phi_j(2) | \psi_1(1) \phi_1(2) \rangle}_{\delta_{j1}} \underbrace{\langle \psi_1(1) \phi_1(2) | \phi_j(2) \rangle}_{\delta_{j1}} = |\psi_1(1)\rangle \langle \psi_1(1)|$$

similarly  $\hat{\rho}_2(2) = \text{Tr}_1 \hat{\rho}(1,2) = |\phi_1(2)\rangle \langle \phi_1(2)|$

$$\hat{\rho}_1(1) \otimes \hat{\rho}_2(2) = |\psi_1(1)\rangle \langle \psi_1(1)| \otimes |\phi_1(2)\rangle \langle \phi_1(2)| = |\psi_1(1) \otimes \phi_1(2)\rangle \langle \psi_1(1) \otimes \phi_1(2)| = \hat{\rho}(1,2)$$

this is readily verified by applying both forms to any basis element  $|\psi_i(1) \phi_j(2)\rangle$  (see slide 1.93)

# Entanglement again

## Exercise 3.3

As in exercise 1.17 (slide 1.99), we consider two spin-1/2 particles in the pure spin-state described by the singlet state vector  $\Psi_S = (1/\sqrt{2}) \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \}$ . The particles separate without interacting with any other system.

a) Calculate the first-order reduced density operator of particle 1 and explain the physical meaning of the result: what do we know about  $s_z(1)$ ?

b) Consider the symmetry of the state vector to write the first-order reduced density operator of particle 2 without performing additional calculations. Does the direct product of the two reduced density operators coincide with the density operator for the whole system? Can we obtain information about the joint observable  $s_z(1)s_z(2)$  from the reduced density operators?

*Results:* a)  $\hat{\rho}_1(1) = \frac{1}{2} |\alpha(1)\rangle\langle\alpha(1)| + \frac{1}{2} |\beta(1)\rangle\langle\beta(1)| = \frac{1}{2} \hat{1}(1)$

b)  $\hat{\rho}_2(2) = \frac{1}{2} |\alpha(2)\rangle\langle\alpha(2)| + \frac{1}{2} |\beta(2)\rangle\langle\beta(2)| = \frac{1}{2} \hat{1}(2)$

$$\hat{\rho}_1(1) \otimes \hat{\rho}_2(2) = \frac{1}{4} (|\alpha\alpha\rangle\langle\alpha\alpha| + |\alpha\beta\rangle\langle\alpha\beta| + |\beta\alpha\rangle\langle\beta\alpha| + |\beta\beta\rangle\langle\beta\beta|) = \frac{1}{4} \hat{1}(1, 2)$$

$$\hat{\rho}(1, 2) = \frac{1}{2} (|\alpha\beta\rangle\langle\alpha\beta| - |\alpha\beta\rangle\langle\beta\alpha| - |\beta\alpha\rangle\langle\alpha\beta| + |\beta\alpha\rangle\langle\beta\alpha|)$$

# Solution of the exercise 3.3

$$a) \hat{\rho} = |\Psi_s\rangle\langle\Psi_s| = \frac{1}{2} |\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle\langle\alpha(1)\beta(2) - \beta(1)\alpha(2)|$$

$$\hat{\rho}_1 = \text{Tr}_2 \hat{\rho}_{(1,2)} = \langle\alpha(2)|\hat{\rho}|\alpha(2)\rangle + \langle\beta(2)|\hat{\rho}|\beta(2)\rangle =$$

$$= \frac{1}{2} \left( \underbrace{\langle\alpha(2)|\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle}_{1} \underbrace{\langle\alpha(1)\beta(2) - \beta(1)\alpha(2)|\alpha(2)\rangle}_{1} + \underbrace{\langle\beta(2)|\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle}_{0} \underbrace{\langle\alpha(1)\beta(2) - \beta(1)\alpha(2)|\beta(2)\rangle}_{0} \right)$$

$$= \frac{1}{2} (|\alpha(1)\rangle\langle\alpha(1)| + |\beta(1)\rangle\langle\beta(1)|) = \frac{1}{2} \hat{1}(1) : \text{mixed state with minimum degree of information}$$

$\Rightarrow$  we have no information about  $\hat{S}_z(1)$  (nor  $S_x(1)$  or  $S_y(1)$ ).

$$b) \hat{\rho}_2 = \frac{1}{2} (|\alpha(2)\rangle\langle\alpha(2)| + |\beta(2)\rangle\langle\beta(2)|) = \frac{1}{2} \hat{1}(2)$$

$$\hat{\rho}_1 \otimes \hat{\rho}_2 = \frac{1}{4} (|\alpha(1)\rangle\langle\alpha(1)| + |\beta(1)\rangle\langle\beta(1)|) \otimes (|\alpha(2)\rangle\langle\alpha(2)| + |\beta(2)\rangle\langle\beta(2)|) =$$

$$= \frac{1}{4} (|\alpha\alpha\rangle\langle\alpha\alpha| + |\alpha\beta\rangle\langle\alpha\beta| + |\beta\alpha\rangle\langle\beta\alpha| + |\beta\beta\rangle\langle\beta\beta|) = \frac{1}{4} \hat{1}_{(1,2)} \quad (\text{of course!})$$

$$\hat{\rho}_{(1,2)} = \frac{1}{2} (|\alpha\beta\rangle\langle\alpha\beta| - |\alpha\beta\rangle\langle\beta\alpha| - |\beta\alpha\rangle\langle\alpha\beta| + |\beta\alpha\rangle\langle\beta\alpha|) \quad *$$

$\hat{\rho}_1$  and  $\hat{\rho}_2$  have no information about individual spins nor joint spin observables like  $S_z(1)S_z(2)$ , while this is completely determined in  $\hat{\rho}_{(1,2)}$ .

# 1-particle or 1<sup>st</sup>-order reduced density matrices

$$\begin{aligned} \rho_1(\vec{x}_1; \vec{x}_1') &\equiv \langle \vec{x}_1 | \hat{\rho}_1(1) | \vec{x}_1' \rangle \\ &= \langle \vec{x}_1 | \text{Tr}_{2\dots N} \hat{\rho}(1, 2, \dots, N) | \vec{x}_1' \rangle \\ &= \int \langle \vec{x}_1, \vec{x}_2, \dots, \vec{x}_N | \hat{\rho}(1, 2, \dots, N) | \vec{x}_1', \vec{x}_2, \dots, \vec{x}_N \rangle d\vec{x}_2 \dots d\vec{x}_N \end{aligned}$$

- If the state is *pure*:  $\hat{\rho}(1, 2, \dots, N) = |\Psi(1, 2, \dots, N)\rangle \langle \Psi(1, 2, \dots, N)|$

$$\rho_1(\vec{x}_1; \vec{x}_1') = \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1', \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_N$$

Indistinguishability:  $\rho_1(\vec{x}; \vec{x}') = \rho_2(\vec{x}; \vec{x}') = \dots = \rho_N(\vec{x}; \vec{x}')$

- *Definition*:  $\gamma(\vec{x}; \vec{x}') \equiv \sum_{i=1}^N \rho_i(\vec{x}; \vec{x}')$   
 $= N \rho_1(\vec{x}; \vec{x}')$   
 $= N \int \Psi(\vec{x}, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}', \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_N$

# One-electron probability density

Probability density of finding **the first** electron in  $\vec{x}$  (in  $\vec{r}$  with spin  $\omega$ )

$$\begin{aligned}\sigma_1(\vec{x}) &= \int |\Psi(\vec{x}, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N)|^2 d\vec{x}_2 d\vec{x}_3 \dots d\vec{x}_N \\ &= \rho_1(\vec{x}; \vec{x})\end{aligned}$$

Probability density of finding **any** electron in  $\vec{x}$ :

$$\begin{aligned}\sigma(\vec{x}) &= \sum_{i=1}^N \sigma_i(\vec{x}) \\ &= N \sigma_1(\vec{x}) \\ &= N \rho_1(\vec{x}; \vec{x}) \\ &= \gamma(\vec{x}; \vec{x}) .\end{aligned}$$

# Other one-electron observables

$$\hat{F}(1, \dots, N) = \sum_{i=1}^N \hat{f}(i)$$

$$\begin{aligned} \langle F \rangle_{\Psi} &= N \langle \Psi | \hat{f}(1) | \Psi \rangle \\ &= N \text{Tr} (\hat{f} \hat{\rho}_1) \end{aligned}$$

$$\langle F \rangle_{\Psi} = \text{Tr} (\hat{f} \hat{\gamma})$$

If the operator has a *diagonal* position representation:

$$\begin{aligned} \langle F \rangle_{\Psi} &= \int \langle \vec{x} | \hat{f} | \vec{x}' \rangle \langle \vec{x}' | \hat{\gamma} | \vec{x} \rangle d\vec{x} d\vec{x}' \quad \leftarrow \quad \langle \vec{x} | \hat{f} | \vec{x}' \rangle = f(\vec{x}) \delta(\vec{x} - \vec{x}') \\ &= \int f(\vec{x}) \gamma(\vec{x}; \vec{x}) d\vec{x} . \end{aligned}$$

# Local one-electron observables

$\hat{p}$  is a *local* operator in position representation:

$$\begin{aligned} \langle \mathbf{x} | \hat{p} \psi \rangle &= (\hat{p}\psi)(\mathbf{x}) \\ &= (-i\hbar d/dx) \psi(\mathbf{x}) \\ &= \hat{p}(\mathbf{x}) \langle \mathbf{x} | \psi \rangle. \end{aligned}$$

For any *local* one-electron operator:  $\langle \vec{x}' | \hat{f}(1) \psi \rangle = \hat{f}(\vec{x}') \langle \vec{x}' | \psi \rangle$

$$\begin{aligned} \langle F \rangle_{\psi} &= \int \langle \vec{x} | \hat{f} \overset{\psi}{\hat{\gamma}} | \vec{x} \rangle d\vec{x} \\ \langle F \rangle_{\psi} &= \int \{f(\vec{x}') \langle \vec{x}' | \hat{\gamma} | \vec{x} \rangle\}_{\vec{x}'=\vec{x}} d\vec{x} \\ &= \int \{f(\vec{x}') \gamma(\vec{x}'; \vec{x})\}_{\vec{x}'=\vec{x}} d\vec{x}, \end{aligned}$$

# Spin-less 1<sup>st</sup>-order reduced density matrix

$$P(\vec{r}; \vec{r}') \equiv \text{Tr}_\omega \gamma(\vec{x}; \vec{x}') = \int_\omega \gamma(\vec{r}\omega; \vec{r}'\omega) d\omega = \gamma(\vec{r}\alpha; \vec{r}'\alpha) + \gamma(\vec{r}\beta; \vec{r}'\beta)$$

- *Pure* states:

$$P(\vec{r}; \vec{r}') = N \int \Psi(\vec{r}\omega, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{r}'\omega, \vec{x}_2, \dots, \vec{x}_N) d\omega d\vec{x}_2 \dots d\vec{x}_N$$

One-electron density:  $\sigma(\vec{r}) \equiv P(\vec{r}; \vec{r})$

- Spin-independent *local* one-electron observables:

$$\hat{F}(\vec{x}_1, \dots, \vec{x}_N) = \sum_{i=1}^N \hat{f}(\vec{r}_i)$$

see [this slide](#)

$$\langle F \rangle_\Psi = \int_{\vec{r}} \int_\omega f(\vec{r}) \gamma(\vec{r}\omega; \vec{r}\omega) d\vec{r} d\omega = \int_{\vec{r}} f(\vec{r}) \underbrace{\int_\omega \gamma(\vec{r}\omega; \vec{r}\omega) d\omega}_{P(\vec{r}; \vec{r})} d\vec{r} = \int_{\vec{r}} f(\vec{r}) \sigma(\vec{r}) d\vec{r}$$

# 2-particle or 2<sup>nd</sup>-order reduced density matrix

$$\hat{\rho}_{12}(1, 2) = \text{Tr}_{3\dots N} \hat{\rho}(1, 2, \dots, N)$$

$$\begin{aligned} \rho_{12}(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') &\equiv \langle \vec{x}_1, \vec{x}_2 | \hat{\rho}_{12}(1, 2) | \vec{x}_1', \vec{x}_2' \rangle = \\ &= \int \langle \vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N | \hat{\rho}(1, \dots, N) | \vec{x}_1', \vec{x}_2', \vec{x}_3, \dots, \vec{x}_N \rangle d\vec{x}_3 \dots d\vec{x}_N \end{aligned}$$

- If the state is pure:

$$\rho_{12}(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') = \int \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi^*(\vec{x}_1', \vec{x}_2', \vec{x}_3, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N$$

*Definition:*

$$\begin{aligned} \Gamma(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') &\equiv N(N-1) \rho_{12}(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') \\ &= N(N-1) \int \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi^*(\vec{x}_1', \vec{x}_2', \vec{x}_3, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N \end{aligned}$$

Why  $N(N-1)$ ?

# Two-electron probability density

Probability density of finding electron 1 in  $\vec{x}_1$  and electron 2 in  $\vec{x}_2$ :

$$\begin{aligned}\sigma_{12}(\vec{x}_1, \vec{x}_2) &= \int |\Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N)|^2 d\vec{x}_3 \dots d\vec{x}_N \\ &= \rho_{12}(\vec{x}_1, \vec{x}_2; \vec{x}_1, \vec{x}_2)\end{aligned}$$

Probability density of finding *any* electrons in  $\vec{x}_1$  and  $\vec{x}_2$ :

$$\begin{aligned}\sigma(\vec{x}_1, \vec{x}_2) &= \underline{\binom{N}{2}} \text{ electron pairs} \\ &= [N(N-1)/2] 2 \sigma_{12}(\vec{x}_1, \vec{x}_2) \\ &= N(N-1) \rho_{12}(\vec{x}_1, \vec{x}_2; \vec{x}_1, \vec{x}_2) \\ &= \Gamma(\vec{x}_1, \vec{x}_2; \vec{x}_1, \vec{x}_2) .\end{aligned}$$

# Other two-electron observables

Two-electron observable:  $\hat{G}(1, \dots, N) = \sum_{i=1}^N \sum_{j>i}^N \hat{g}(i, j)$

$$\begin{aligned} \langle \mathbf{G} \rangle_{\Psi} &= [N(N-1)/2] \langle \Psi | \hat{g}(1, 2) | \Psi \rangle \\ &= [N(N-1)/2] \text{Tr} \{ \hat{g}(1, 2) \hat{\rho}_{12}(1, 2) \} \end{aligned}$$

$$\langle \mathbf{G} \rangle_{\Psi} = \frac{1}{2} \text{Tr} (\hat{g} \hat{\Gamma})$$

Coordinate representation:  $\langle \mathbf{G} \rangle_{\Psi} = (1/2) \int \langle \vec{x}_1, \vec{x}_2 | \hat{g} \hat{\Gamma} | \vec{x}_1, \vec{x}_2 \rangle d\vec{x}_1 d\vec{x}_2$

# Spin-less 2<sup>nd</sup>-order reduced density matrix

$$\begin{aligned} P(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2) &= \text{Tr}_{\omega_1 \omega_2} \Gamma(\vec{x}_1', \vec{x}_2'; \vec{x}_1, \vec{x}_2) \\ &= \int \Gamma(\vec{r}_1' \omega_1, \vec{r}_2' \omega_2; \vec{r}_1 \omega_1, \vec{r}_2 \omega_2) d\omega_1 d\omega_2 \end{aligned}$$

$$\langle \mathbf{G} \rangle_{\Psi} = (1/2) \int (\hat{g}(\vec{r}_1', \vec{r}_2') P(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2))_{\vec{r}_1'=\vec{r}_1, \vec{r}_2'=\vec{r}_2} d\vec{r}_1 d\vec{r}_2$$

Diagonal operator in the position representation:

$$\langle \mathbf{G} \rangle_{\Psi} = (1/2) \int g(\vec{r}_1, \vec{r}_2) \sigma(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

where  $\sigma(\vec{r}_1, \vec{r}_2) \equiv P(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)$

# Total non-relativistic electronic energy

*Example:*

The expected value of the non-relativistic electronic hamiltonian of a molecule with M nuclei and N electrons:

$$\hat{H} = \sum_i^N (-1/2) \nabla_i^2 - \sum_A^M \sum_i^N Z_A r_{iA}^{-1} + \sum_{j>i}^N r_{ij}^{-1}$$

can be cast into the form:

$$E = (-1/2) \int \{\nabla'^2 P(\vec{r}'; \vec{r})\}_{\vec{r}'=\vec{r}} d\vec{r} - \sum_A^M Z_A \int r_{1A}^{-1} \sigma(\vec{r}_1) d\vec{r}_1 + (1/2) \int r_{12}^{-1} \sigma(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

**Much less information than  $\Psi(1, 2, \dots, N)$  is needed!!!**

# Discrete representations of reduced density operators

- **Continuous** reduced density matrices are useful for theoretical developments (they are exact representations of the corresponding operators).
- **Discrete** representations are useful for computational purposes (the fidelity of the representation depends on the degree of completeness of the chosen basis set).
- Orthonormal spin-orbital basis set:  $\{\dots \psi_i \dots\}$

$$\begin{aligned}
 (\Upsilon_\psi)_{ij} &= \langle \psi_i | \hat{\gamma} | \psi_j \rangle \\
 &= \int \langle \psi_i | \boxed{\vec{x}} \rangle \langle \vec{x} | \hat{\gamma} \boxed{\vec{x}'} \rangle \langle \vec{x}' | \psi_j \rangle \boxed{d\vec{x}} \boxed{d\vec{x}'} \\
 &= \int \psi_i^*(\vec{x}) \gamma(\vec{x}; \vec{x}') \psi_j(\vec{x}') d\vec{x} d\vec{x}' \\
 (\Gamma_\psi)_{ij, kl} &= \langle \psi_i \psi_j | \Gamma \psi_k \psi_l \rangle \\
 &= \int \psi_i^*(\vec{x}_1) \psi_j^*(\vec{x}_2) \Gamma(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') \psi_k(\vec{x}_1') \psi_l(\vec{x}_2') d\vec{x}_1 d\vec{x}_2 d\vec{x}_1' d\vec{x}_2'
 \end{aligned}$$

# Reverse transformations

If the basis set  $\{\dots\psi_i\dots\}$  set is orthonormal and complete:

$$\begin{aligned}
 \gamma(\vec{x}; \vec{x}') &= \langle \vec{x} | \hat{\gamma} \vec{x}' \rangle \\
 &= \sum_{ij} \langle \vec{x} | \psi_i \rangle \langle \psi_i | \hat{\gamma} \psi_j \rangle \langle \psi_j | \vec{x}' \rangle \\
 &= \boldsymbol{\psi}(\vec{x}) \boldsymbol{\gamma}_\psi \boldsymbol{\psi}^\dagger(\vec{x}') . \\
 &= \begin{pmatrix} \psi_1(\vec{x}) & \dots & \psi_i(\vec{x}) & \dots \end{pmatrix} \begin{pmatrix} \gamma_{11} & \dots & \gamma_{1j} & \dots \\ \dots & \dots & \dots & \dots \\ \gamma_{i1} & \dots & \gamma_{ij} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \psi_1^*(\vec{x}') \\ \dots \\ \psi_j^*(\vec{x}') \\ \dots \end{pmatrix}
 \end{aligned}$$

$$\Gamma(\vec{x}_1, \vec{x}_2; \vec{x}_1', \vec{x}_2') = \sum_{ijkl} \psi_i(\vec{x}_1) \psi_j(\vec{x}_2) (\boldsymbol{\Gamma}_\psi)_{ij, kl} \psi_k^*(\vec{x}_1') \psi_l^*(\vec{x}_2')$$

# Expected values in terms of discrete reduced density matrices

$$\begin{aligned}
 \langle F \rangle &= \text{Tr} (\mathbf{f} \boldsymbol{\gamma}_\psi) \\
 &= \sum_{ij} f_{ij} (\boldsymbol{\gamma}_\psi)_{ji} \\
 \langle G \rangle &= (1/2) \text{Tr} (\mathbf{g} \boldsymbol{\Gamma}_\psi) \\
 &= \sum_{ijkl} g_{ij, kl} (\boldsymbol{\Gamma}_\psi)_{kl, ij}
 \end{aligned}$$

where

$$g_{ij, kl} = \langle \psi_i \psi_j | \hat{g} | \psi_k \psi_l \rangle$$

# Natural spin-orbitals

The eigenvectors of  $\hat{\gamma}$ :  $\hat{\gamma} \eta_i = n_i \eta_i$  are called *natural spin-orbitals*.

Spectral decomposition of  $\hat{\gamma}$ :  $\hat{\gamma} = \sum_i n_i |\eta_i\rangle \langle \eta_i|$

$$\hat{\rho}_1 = \frac{\hat{\gamma}}{N} = \sum_i \frac{n_i}{N} |\eta_i\rangle \langle \eta_i|$$

$\Rightarrow n_i/N$  represents the probability that **one particular** electron is in the pure state  $\eta_i$ , and  $n_i$  is the probability that **any** electron is in  $\eta_i$ , that is, the *occupation number of  $\eta_i$* .

- *Mixed state*: the 1- $e^-$  state is not completely determined because of the (averaged) influences of the other  $e^-$ s (exact  $\neq$  HF approx.).
- *Fastest convergence of CI*.
- *Singlet diradicals* in multiconfig. wf (spin-density = 0 everywhere).

# 2nd quantized form

## Exercise 3.4

**a)** Show that, if  $\phi_r$  and  $\phi_s$  are orthonormal spin-orbitals, then  $|\phi_r\rangle \langle\phi_s| = \hat{a}_r^\dagger \hat{a}_s$  (restricted to  $\mathcal{H}_1$ ).

**b)** Show that the second quantized form of  $\hat{\gamma}$  in an arbitrary orthonormal spin-orbital basis set is

$$\hat{\gamma} = \sum_{rs} \gamma_{rs} \hat{a}_r^\dagger \hat{a}_s$$

and, for the natural spin-orbital basis,

$$\hat{\gamma} = \sum_i n_i \hat{a}_i^\dagger \hat{a}_i = \sum_i n_i \hat{n}_i$$

## Solution of the exercise 3.4

a) Slide 2.10:  $\hat{\gamma} = \sum_{rs} \gamma_{rs} |\phi_r\rangle \langle \phi_s|$ ,  $\{|\phi_r\rangle\}$  orthonormal

$$|\phi_r\rangle \langle \phi_s| \stackrel{?}{=} \hat{a}_r^\dagger \hat{a}_s \quad (\text{restricted to } \mathcal{R}_1)$$

let's apply both operators to any basis vector  $\phi_i$ :

$$|\phi_r\rangle \langle \phi_s | \phi_i \rangle = \delta_{si} |\phi_r\rangle$$

$$\hat{a}_r^\dagger \hat{a}_s |\phi_i\rangle = \hat{a}_r^\dagger \delta_{si} (-1)^0 |i\rangle = \delta_{si} |\phi_r\rangle$$

b) Slide 2.10 + a):  $\hat{\gamma} = \sum_{rs} \gamma_{rs} \hat{a}_r^\dagger \hat{a}_s$

Spectral decomposition of  $\hat{\gamma}$ :

$$\hat{\gamma} = \sum_i n_i \hat{P}_{n_i} = \sum_i^{\text{all the eigenvectors}} n_i |\eta_i\rangle \langle \eta_i| = \sum_i^{\text{eigenvect}} n_i \hat{a}_i^\dagger \hat{a}_i = \sum_i^{\text{eigenvect}} n_i \hat{n}_i$$