Quantum embedding in electronic structure theory

Part 2: Concept of embedding and its various formulations

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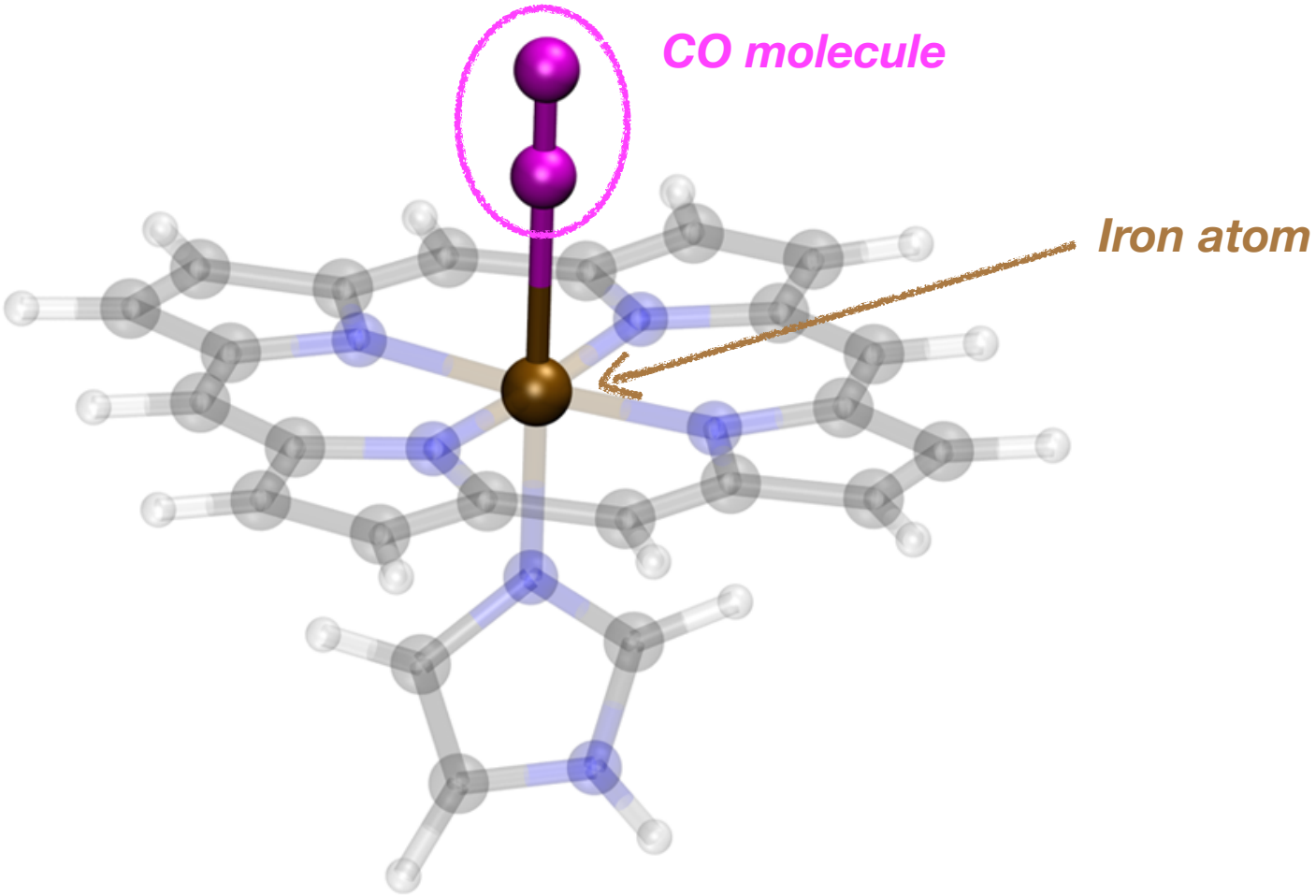
CO Binding in an Iron–Porphyrin Complex



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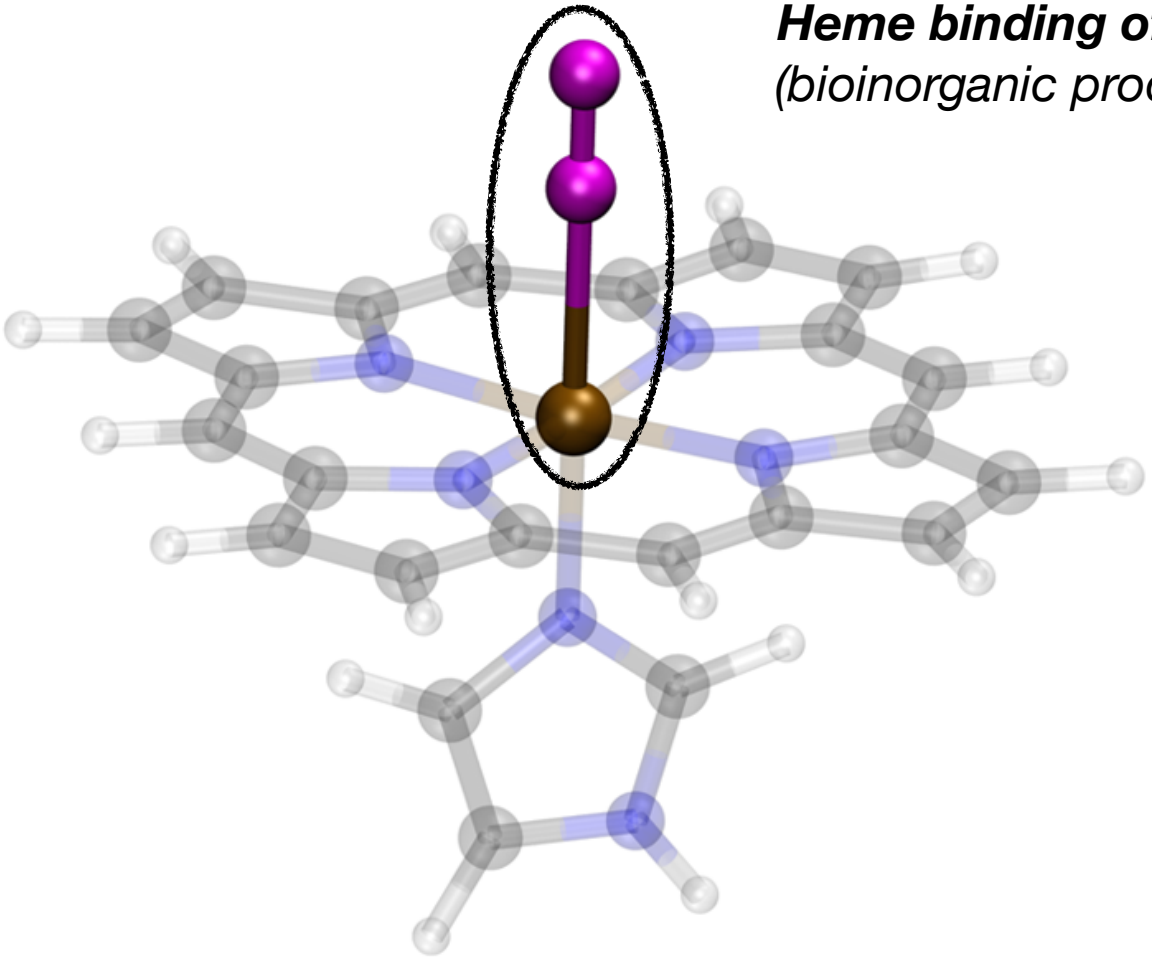
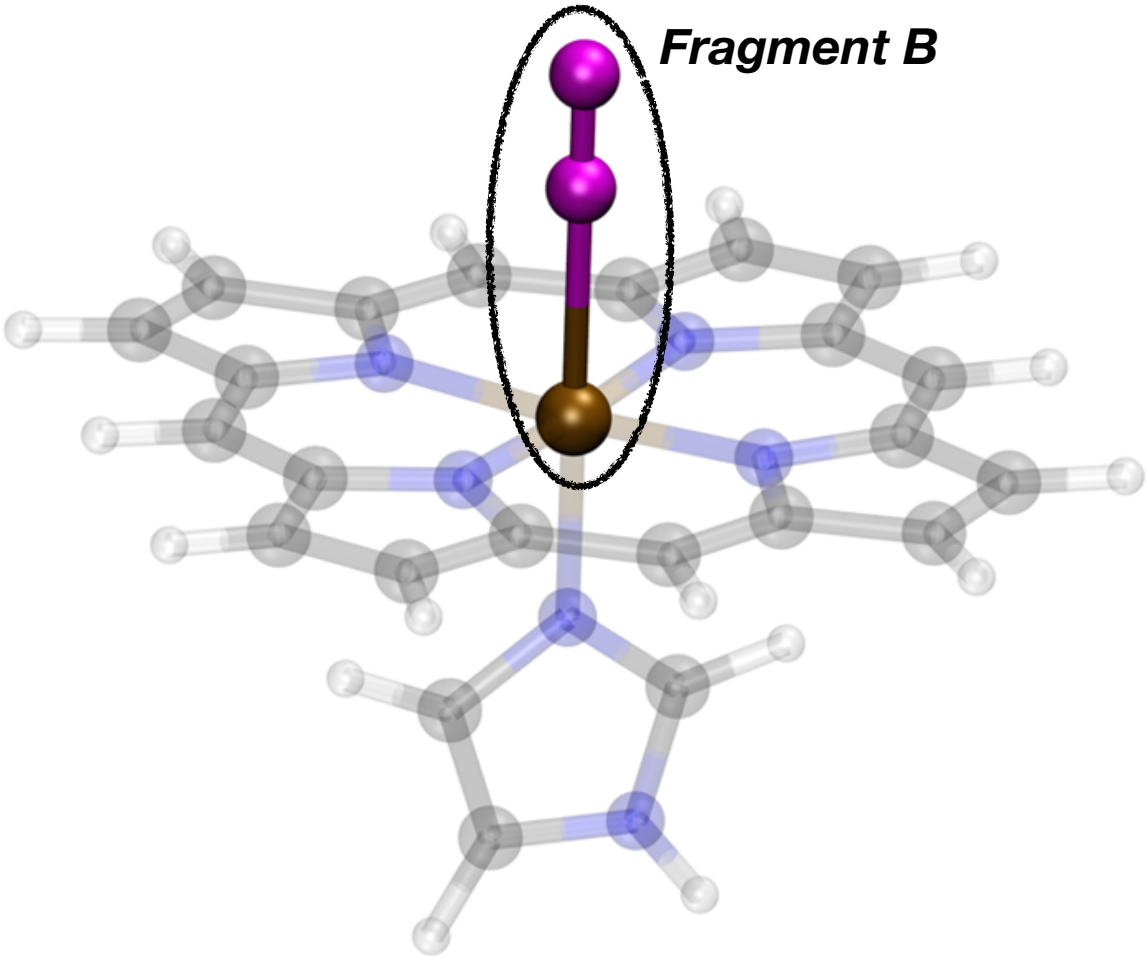


Heme binding of CO
(bioinorganic process)

*M. E. Fornace et al., J. Chem. Theory Comput. 2015, **11**, 568–580*

CO Binding in an Iron–Porphyrin Complex



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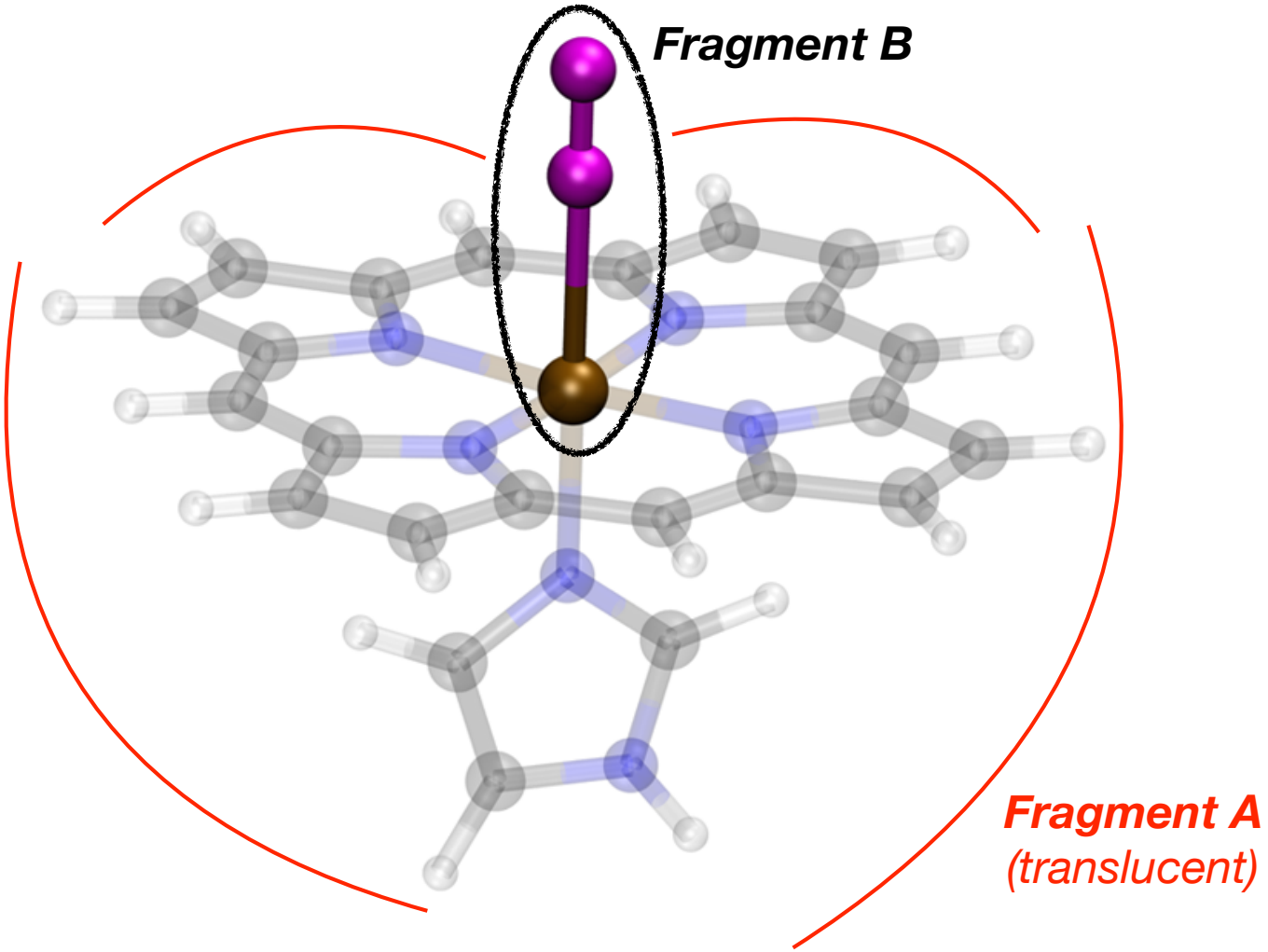
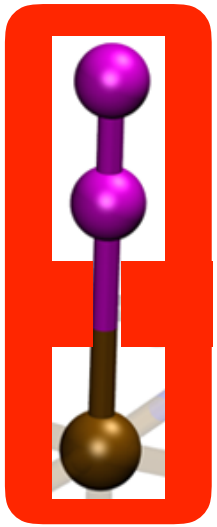
CO Binding in an Iron–Porphyrin Complex

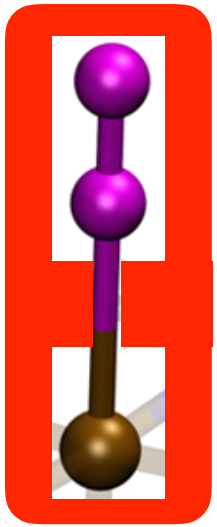


CO Binding in an Iron–Porphyrin Complex



To-be-described embedded fragment B

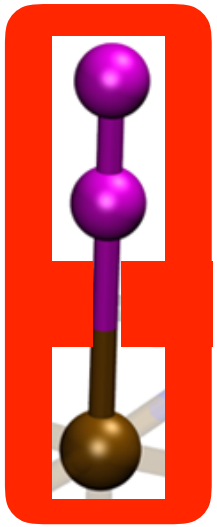
CO Binding in an Iron–Porphyrin Complex



To-be-described embedded fragment B

$$\hat{H}^{emb}\Psi_B = \mathscr{E}_B\Psi_B$$

CO Binding in an Iron–Porphyrin Complex



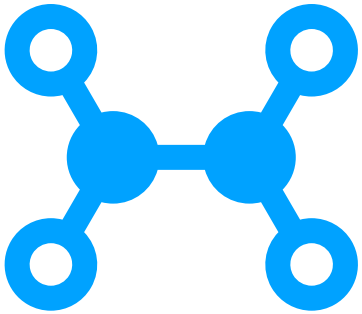
To-be-described embedded fragment B

$$\hat{H}^{emb}\Psi_B = \mathscr{E}_B\Psi_B$$

?

Strategy 1: DFT-based quantum embedding approach

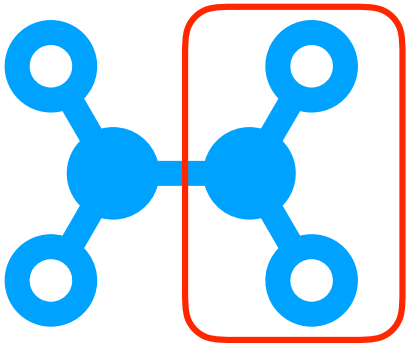
Frozen density embedding theory



$$n_0(\mathbf{r}) = ?$$

Frozen density embedding theory

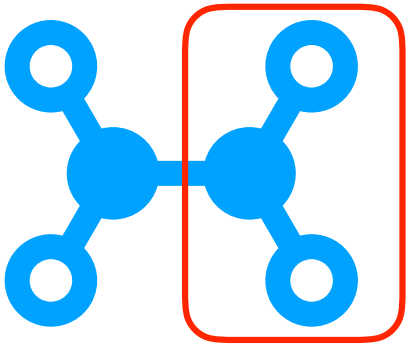
Fragment A



$n_A(\mathbf{r})$ ⟵ *Density giving an approximate description of a molecular fragment*

Frozen density embedding theory

Fragment A



$n_A(\mathbf{r})$

Density giving an approximate description of a molecular fragment

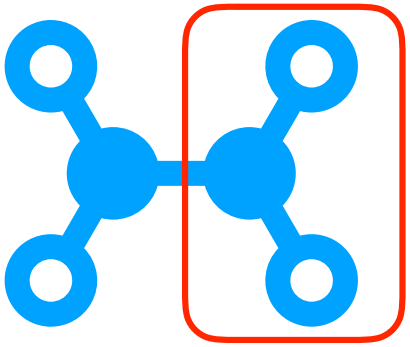
Total number of electrons in the molecule

$$\int d\mathbf{r}\, n_A(\mathbf{r}) = N_A < N$$

*Wesolowski, T. A.; Warshel, A., J. Phys. Chem. 1993, **97**, 8050–8053.*

Frozen density embedding theory

Fragment A



$n_A(\mathbf{r})$

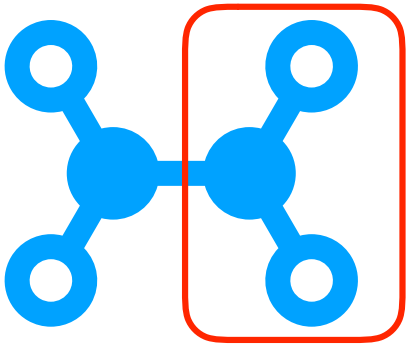
Density *giving an approximate description of a molecular* *fragment*

Fixed *in the theory (hence the name* *“frozen density”)*

Wesolowski, T. A.; Warshel, A., J. Phys. Chem. 1993, ***97****, 8050–8053.*

Frozen density embedding theory

Fragment A



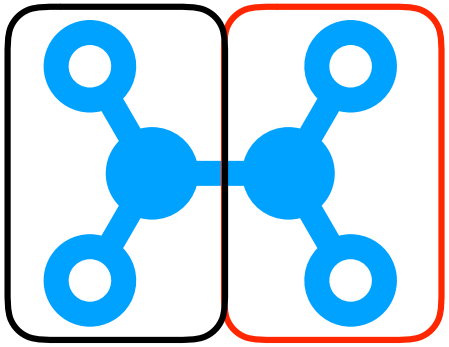
$n_A(\mathbf{r})$

Density giving an approximate description of a molecular fragment

*Used as **reference density***

Frozen density embedding theory

Fragment B **Fragment A**



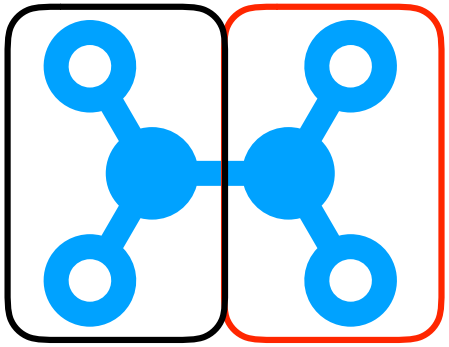
$n_A(\mathbf{r})$ ***known***

$$n_B(\mathbf{r}) = n_0(\mathbf{r}) - n_A(\mathbf{r}) = ?$$

Wesolowski, T. A.; Warshel, A., J. Phys. Chem. 1993, ***97****, 8050–8053.*

Frozen density embedding theory

Fragment B **Fragment A**

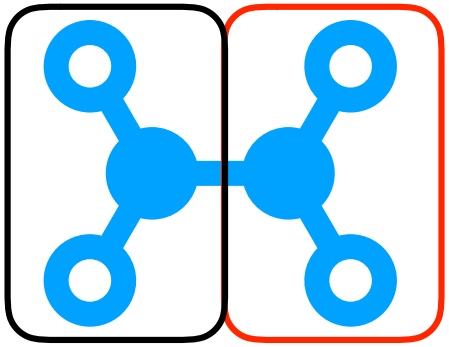


$n_A(\mathbf{r})$ ***known***

$$n_B(\mathbf{r}) = n_0(\mathbf{r}) - n_A(\mathbf{r}) \overset{assumption}{\equiv} n_{\Psi_B}$$

Frozen density embedding theory

Fragment B **Fragment A**

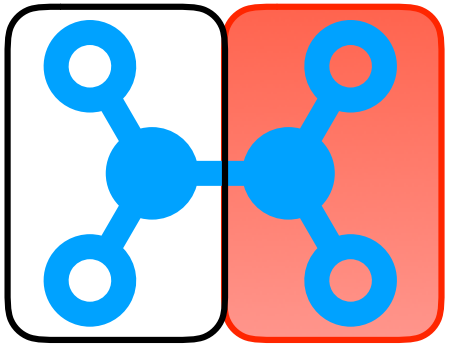


$n_A(\mathbf{r})$ ***known***

$$n_B(\mathbf{r}) = n_0(\mathbf{r}) - n_A(\mathbf{r}) \overset{assumption}{\equiv} n_{\Psi_B} = ?$$

Frozen density embedding theory

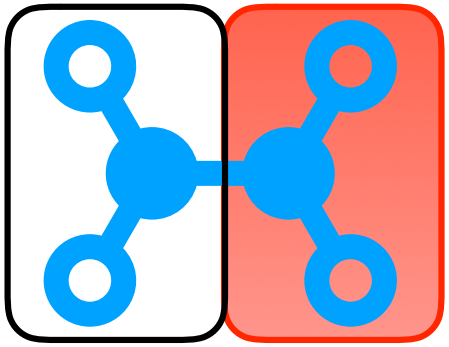
Fragment B



unknown $\Psi_B = ?$ $n_A(\mathbf{r})$ ***known***

Frozen density embedding theory

Fragment B



unknown $\Psi_B = ?$ $n_A(\mathbf{r})$ ***known***

Fragment B is ***embedded*** into the density-functional fragment A

Variational principle for fragment B

$$E_0 = \min_n \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_{n_B \to N - N_A} \left\{ F[n_B + n_A] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r})$$

$n = n_B + n_A$

Frozen (*i.e.*, fixed)

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_{n_B \to N - N_A} \left\{ F[n_B + n_A] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r})$$

Less electrons *are now treated explicitly*

Frozen (*i.e.,* fixed)

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

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$$= \min_{n_B \to N - N_A} \left\{ F[n_B] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) + \Delta F[n_B, n_A] \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) + F[n_A]$$

$$F[n_B + n_A] = F[n_B] + F[n_A] + \Delta F[n_B, n_A]$$

Formal decomposition

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_{n_B \to N - N_A} \left\{ F[n_B + n_A] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r})$$

$$= \min_{n_B \to N - N_A} \left\{ F[n_B] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) + \Delta F[n_B, n_A] \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) + F[n_A]$$

*Bifunctional describing the **coupling** between the two fragments*

$$F[n_B + n_A] = F[n_B] + F[n_A] + \Delta F[n_B, n_A]$$

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_{n_B \to N - N_A} \left\{ F[n_B + n_A] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r})$$

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$$\min_{n_B \to N - N_A} \left\{ \min_{\Psi \to n_B} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle \right\} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_B(\mathbf{r}) + \Delta F[n_B, n_A] \right\}$$

Variational principle for fragment B

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

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Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] \;=\; \min_{\Psi \to N - N_A} \left\{ \langle \Psi \,|\, \hat{H} \,|\, \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

Analogous to solving
the Schrödinger equation for ***fragment B***
in the presence of ***fragment A***

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

Embedding density functional

$$\Delta F[n_B, n_A] = F[n_B + n_A] - F[n_B] - F[n_A]$$

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

$$\Delta F[n_B, n_A] = F[n_B + n_A] - F[n_B] - F[n_A]$$

$$= E_{\text{Hxc}}[n_B + n_A] - E_{\text{Hxc}}[n_B] - E_{\text{Hxc}}[n_A]$$

$$+ T_{\text{s}}[n_B + n_A] - T_{\text{s}}[n_B] - T_{\text{s}}[n_A]$$

KS decompositions

$$F[n] = T_{\text{s}}[n] + E_{\text{Hxc}}[n]$$

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

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$$= E_{\text{Hxc}}[n_B + n_A] - E_{\text{Hxc}}[n_B] - E_{\text{Hxc}}[n_A]$$

Evaluated from xc ***density-functional approximations*** *(DFAs)*

$$+ T_{\text{s}}[n_B + n_A] - T_{\text{s}}[n_B] - T_{\text{s}}[n_A]$$

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

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Described with KS orbitals
in KS-DFT

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

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$$+ T_{\text{s}}[n_B + n_A] - T_{\text{s}}[n_B] - T_{\text{s}}[n_A]$$

Implicit *functional of the density*

↓

Described with KS orbitals *in KS-DFT*

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

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$$+ T_{\text{s}}[n_B + n_A] - T_{\text{s}}[n_B] - T_{\text{s}}[n_A]$$

More difficult
to approximate with density functionals

Variational principle for fragment B

$$E_0 - \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n_A(\mathbf{r}) - F[n_A] = \min_{\Psi \to N - N_A} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \Delta F[n_\Psi, n_A] \right\}$$

$$\Delta F[n_B, n_A] = F[n_B + n_A] - F[n_B] - F[n_A]$$

$$= E_{\text{Hxc}}[n_B + n_A] - E_{\text{Hxc}}[n_B] - E_{\text{Hxc}}[n_A]$$

$$+ T_{\text{s}}[n_B + n_A] - T_{\text{s}}[n_B] - T_{\text{s}}[n_A]$$

challenging task!

More difficult
to approximate with density functionals

Strategy 2: Quantum embedding in the N-electron space

Strategy 2: Quantum embedding in the N-electron space

*We will use **second quantization** in the following.*

https://www.youtube.com/watch?v=FQBrEI57pDA

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

Usually Hartree-Fock (HF) spin-orbitals

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

Usually Hartree-Fock (HF) spin-orbitals

$\{\chi_\nu(\mathbf{x})\}_{\nu=A,B,\ldots}$ ⟵ ***Atomic spin-orbitals centered on the nuclei*** $A, B, \ldots$

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

Usually Hartree-Fock (HF) spin-orbitals

$\{\chi_\nu(\mathbf{x})\}_{\nu=A,B,\ldots}$ ← ***Atomic spin-orbitals centered on the nuclei*** $A, B, \ldots$

$$\varphi_P(\mathbf{x}) = \sum_{\nu}^{nuclei} C_{\nu P}\,\chi_\nu(\mathbf{x})$$

Schrödinger equation in second quantization

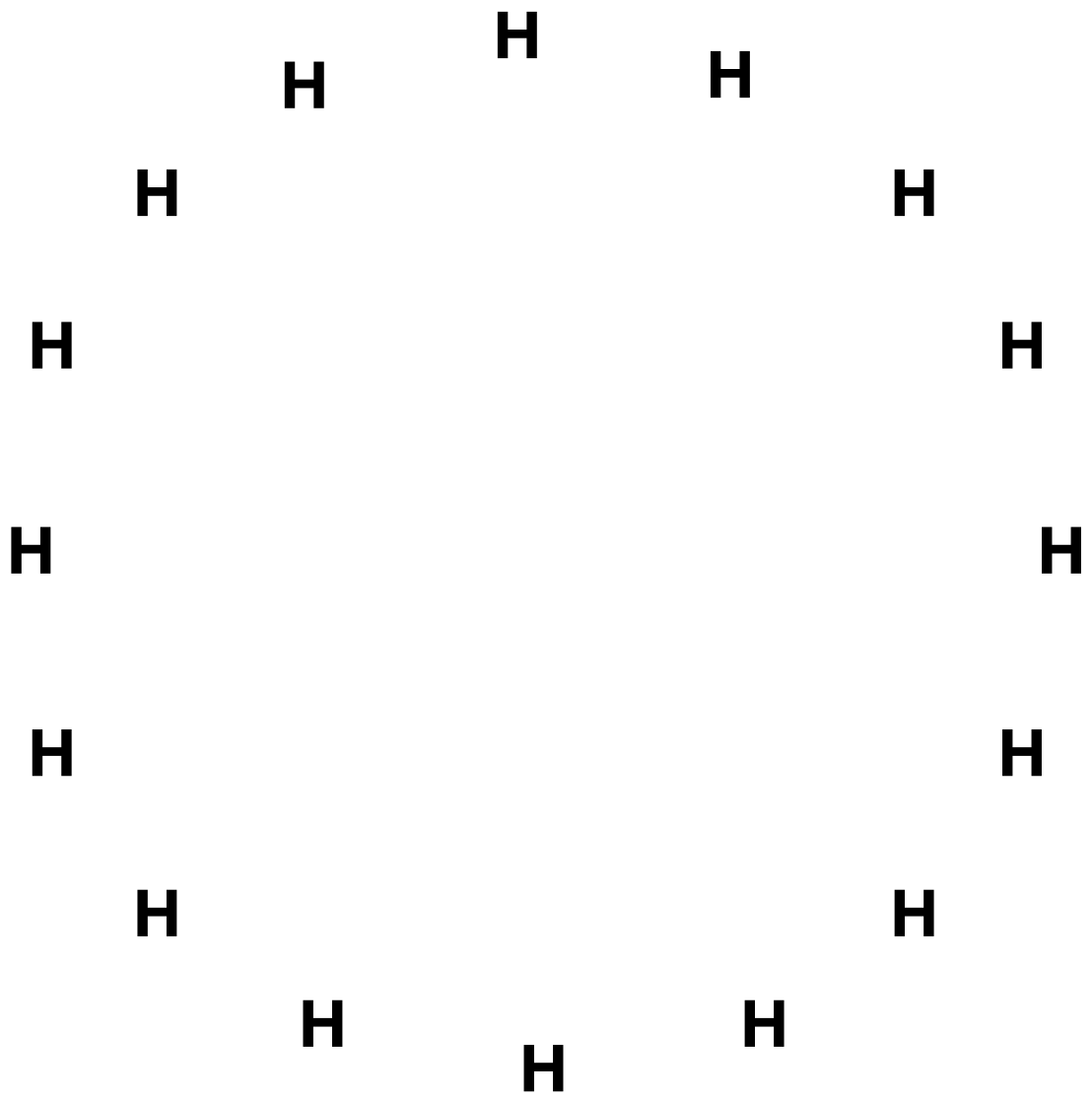
$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

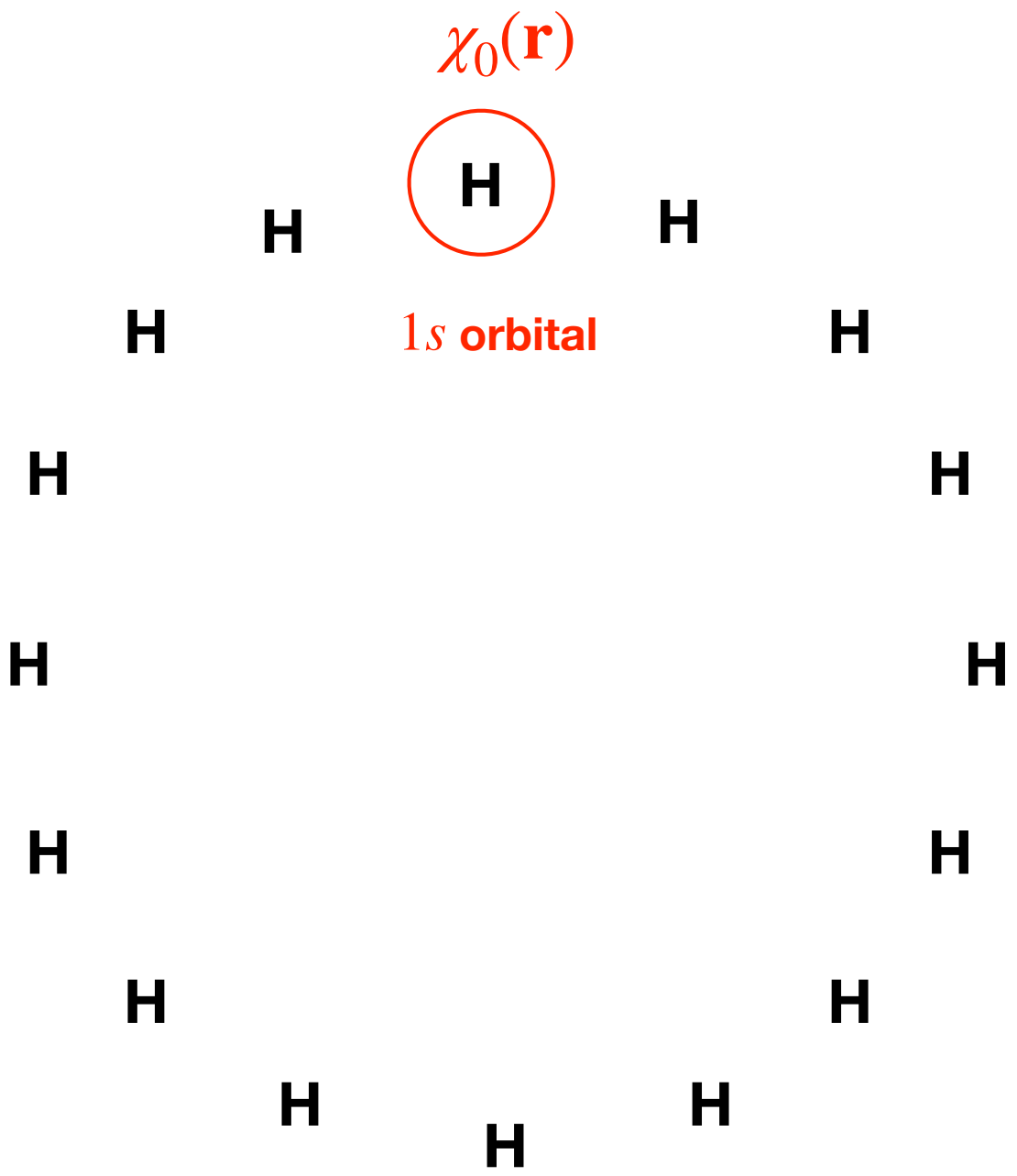
Optimised through energy minimisation

$$\varphi_P(\mathbf{x}) = \sum_{\nu}^{nuclei} C_{\nu P}\,\chi_\nu(\mathbf{x})$$

Prototypical ring of $L = 16$ hydrogen atoms



Prototypical ring of $L = 16$ hydrogen atoms



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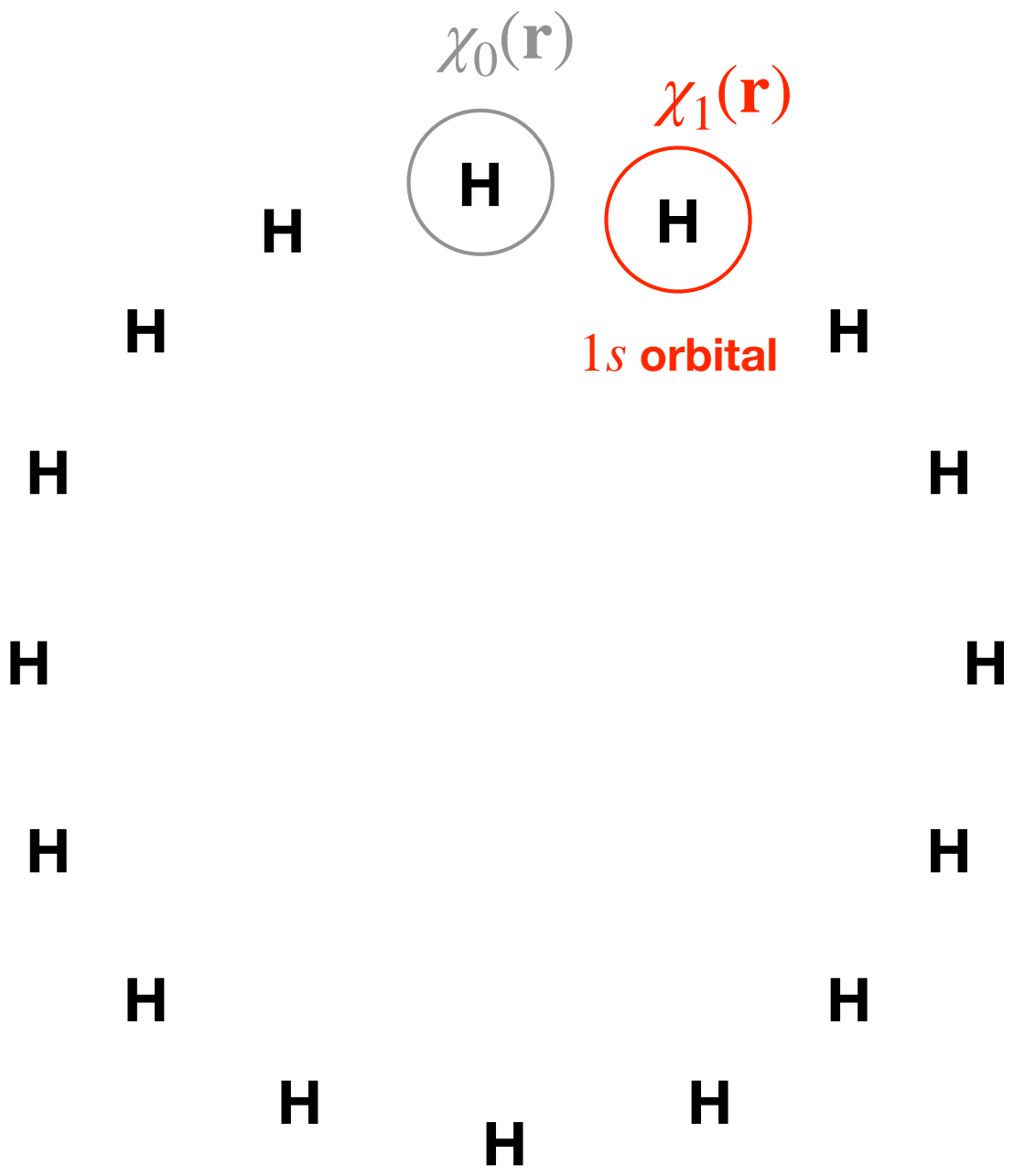
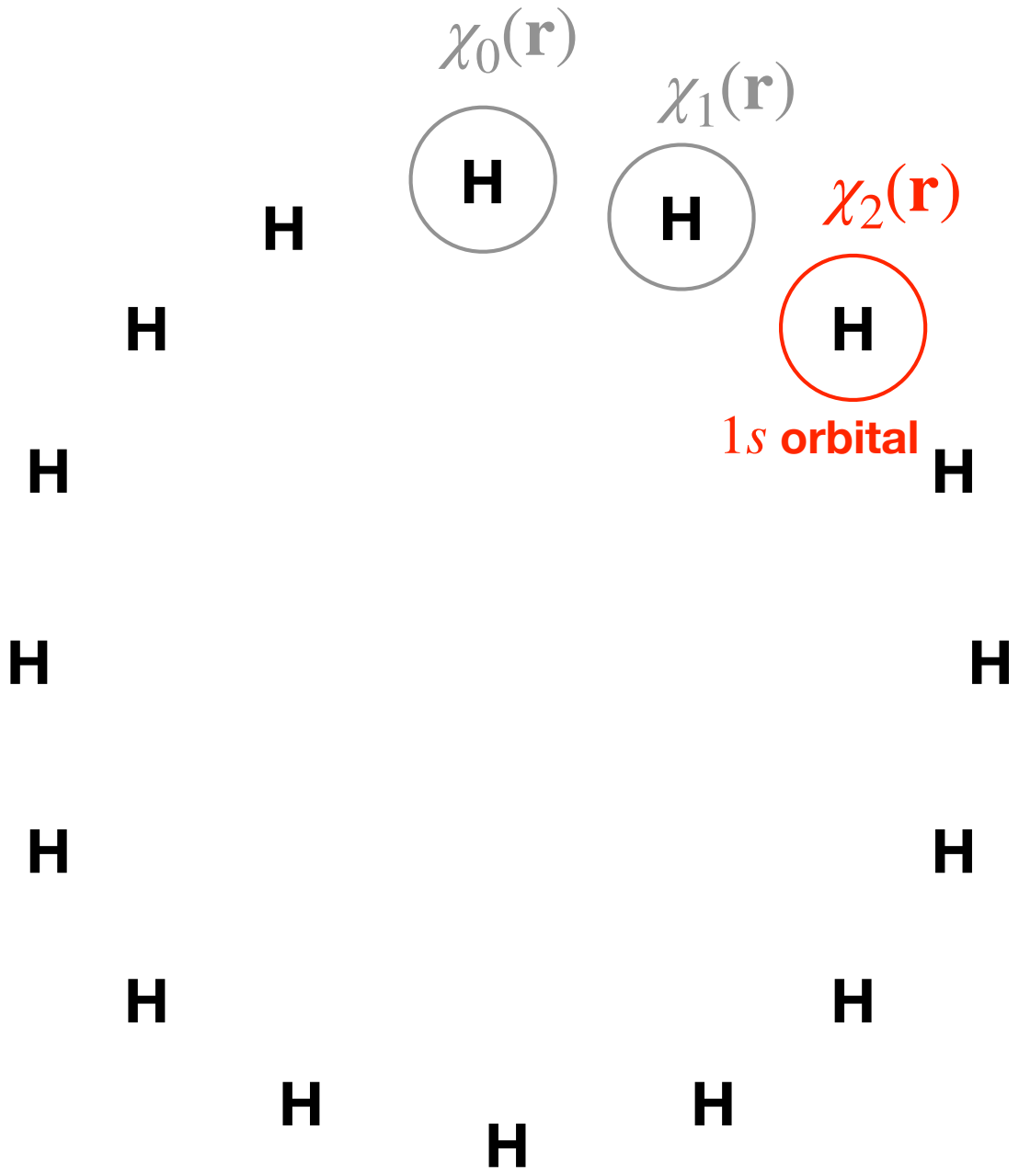


Prototypical ring of $L = 16$ hydrogen atoms



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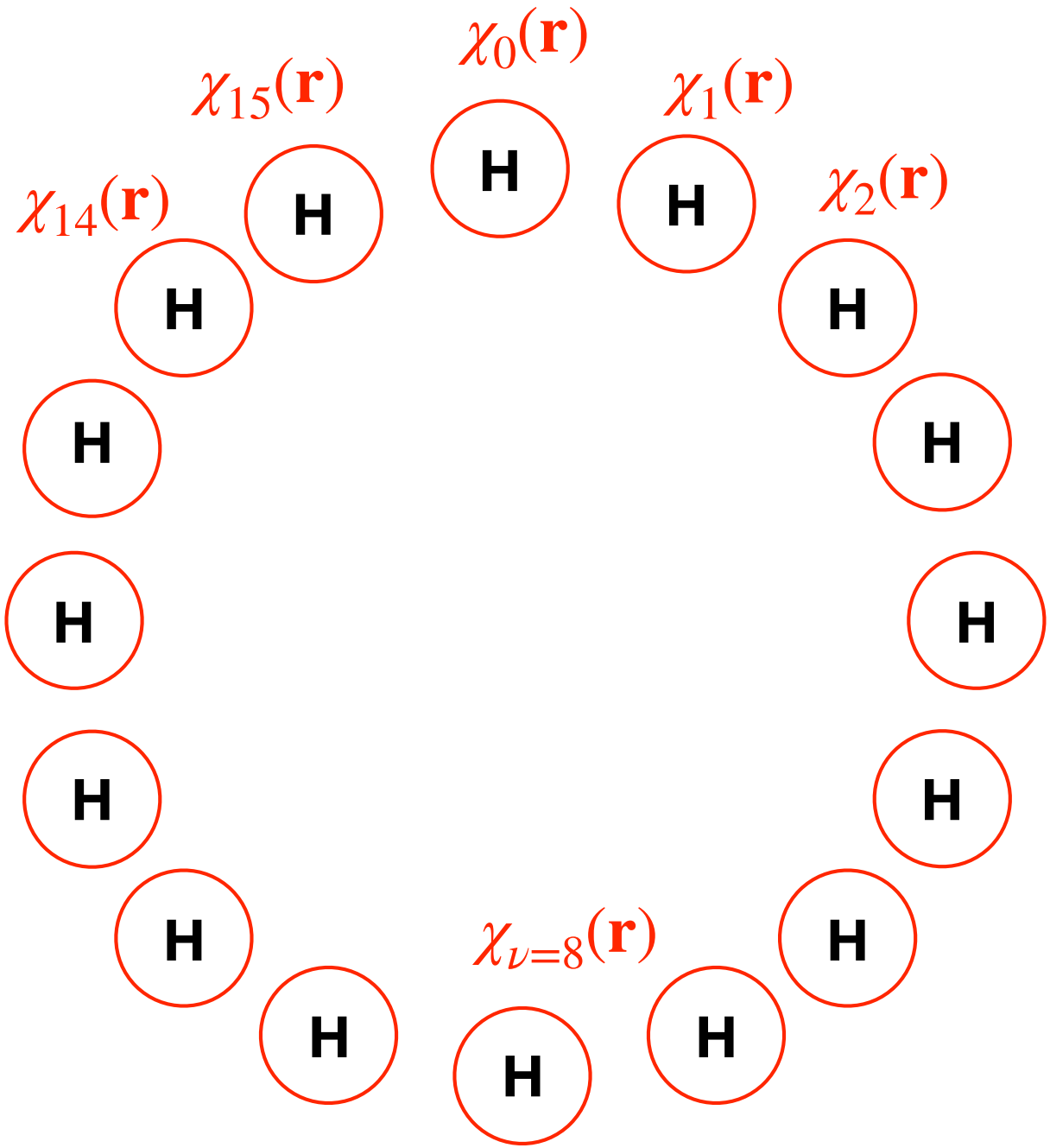
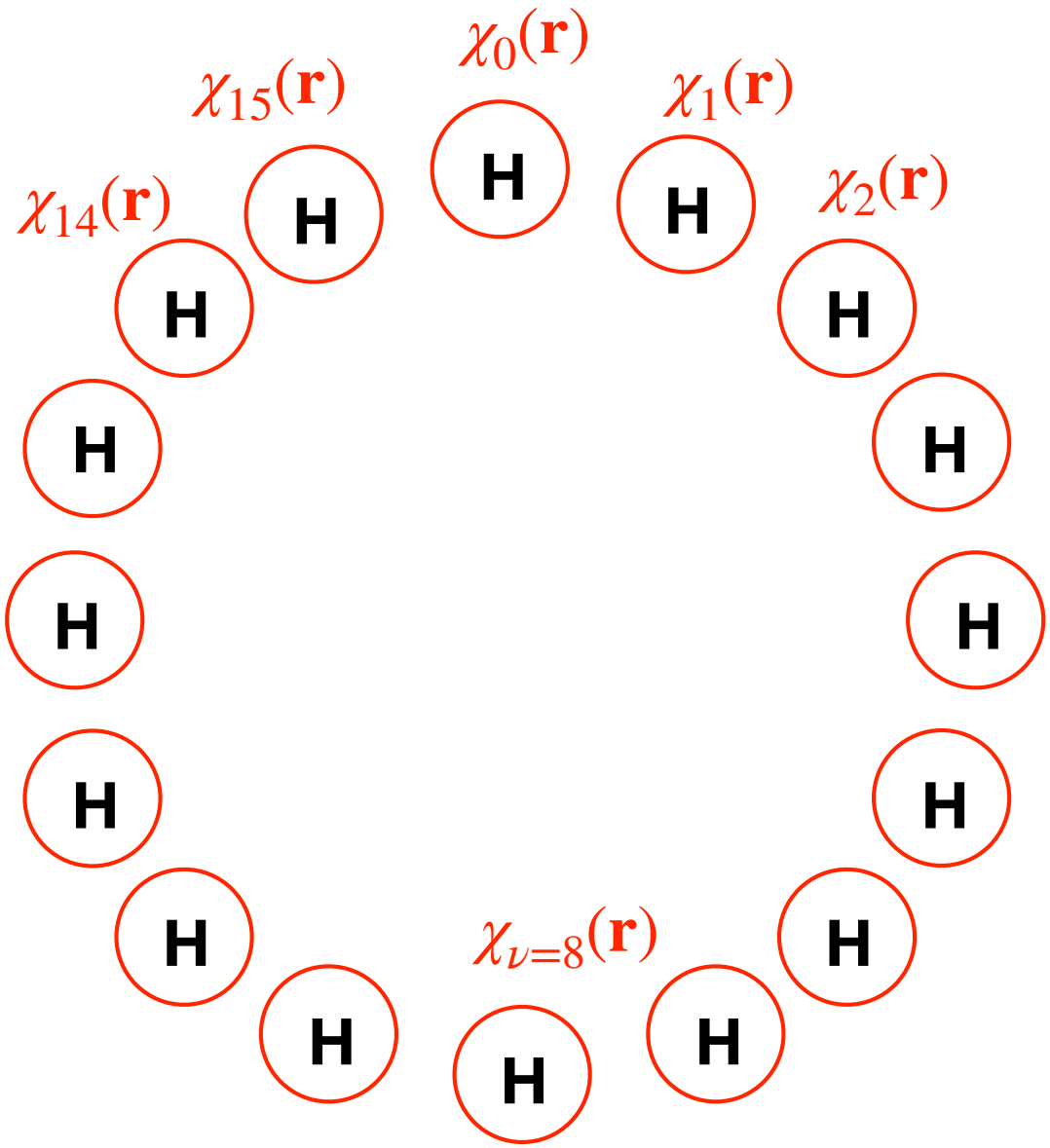


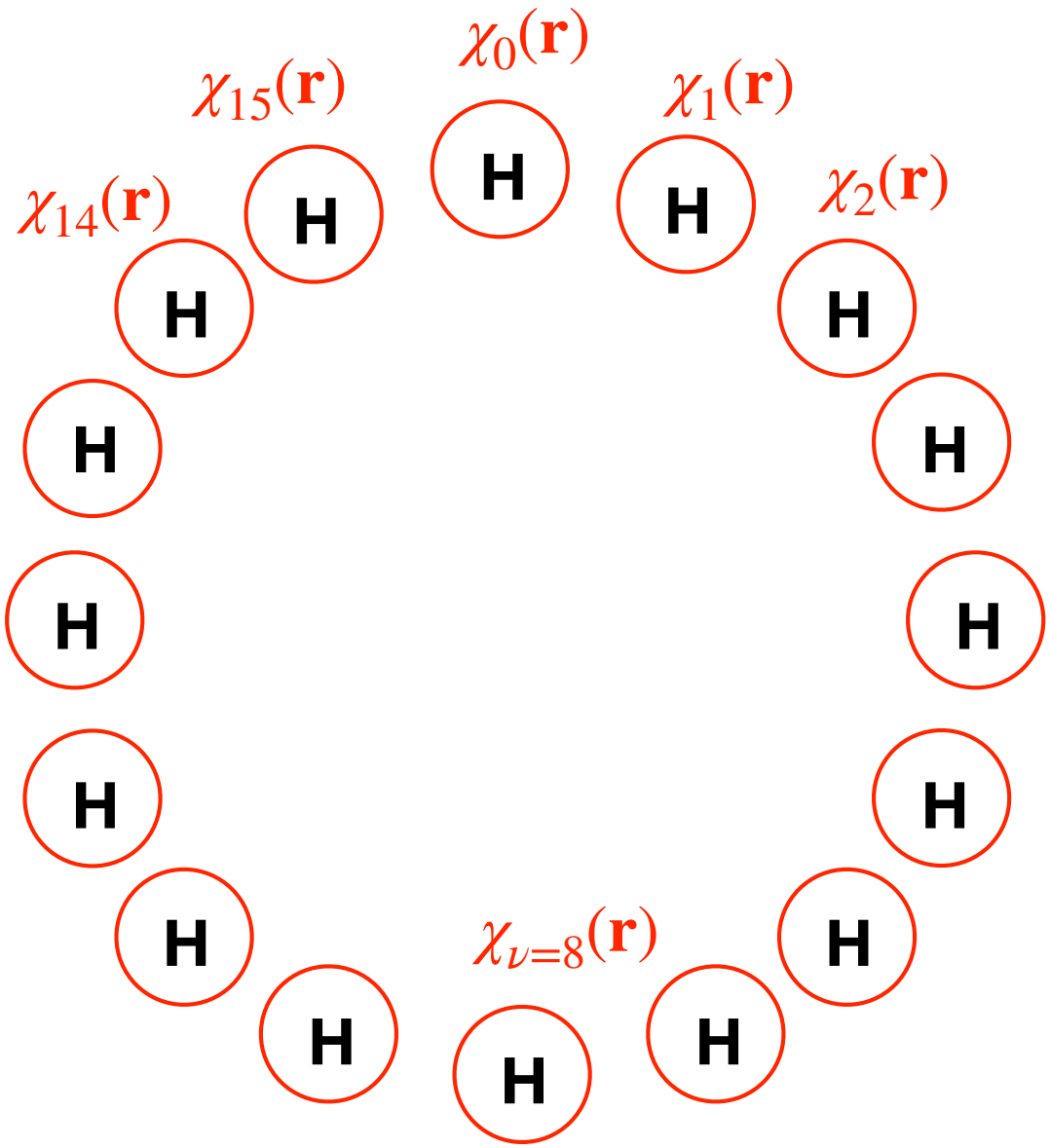
Prototypical ring of $L = 16$ hydrogen atoms



Molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_{\nu=0}^{15} C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Prototypical ring of $L = 16$ hydrogen atoms



Molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_{\nu} C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Delocalised over the ring

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

***Step 2**: Implement the Hamiltonian in second quantization in that basis*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

See the video for further explanations*

**https://www.youtube.com/watch?v=FQBrEI57pDA*

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$$\int d\mathbf{x}\, \varphi_P(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \varphi_Q(\mathbf{x})$$

One-electron integrals

Schrödinger equation in second quantization

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Two-electron integrals

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2 \; \varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_R(\mathbf{x}_1)\varphi_S(\mathbf{x}_2)$$

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

Step 1: *Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

Step 2: *Implement the Hamiltonian in second quantization in that basis*

Step 3: *Determine variationally the ground-state wave function expansion in the corresponding* N*-electron basis*

$$|\Psi_0\rangle \equiv \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N}\ \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}\,|\,\mathrm{vac}\rangle$$

Schrödinger equation in second quantization

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Distribute N ***electrons in*** $\mathscr{M}$ ***spin-orbitals!***

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

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Slater determinant

Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

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Configuration Interaction (CI) coefficient

Configuration interaction (CI) method

$$|\Psi_0\rangle \equiv \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N} \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

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CI coefficient

$$\equiv \sum_{\mathcal{J}}^{determinants} C_{\mathcal{J}}|\det_{\mathcal{J}}\rangle$$

Configuration interaction (CI) method

$$|\Psi_0\rangle \equiv \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N} \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

$$\equiv \sum_{\mathcal{J}}^{determinants} C_{\mathcal{J}}|\det_{\mathcal{J}}\rangle$$

Known

Configuration interaction (CI) method

$$|\Psi_0\rangle \equiv \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N}\ \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

$$\equiv \sum_{\mathcal{I}}^{determinants} C_{\mathcal{I}}|\det_{\mathcal{I}}\rangle$$

Orthonormal basis of N-electron states

$$\langle \det_{\mathcal{I}}|\det_{\mathcal{L}}\rangle = \delta_{\mathcal{I}\mathcal{L}}$$

Configuration interaction (CI) method

$$|\Psi_0\rangle \equiv \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N}\ \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

$$\equiv \sum_{\mathcal{J}}^{determinants} C_{\mathcal{J}}|\det{}_{\mathcal{J}}\rangle$$

Unknown

Configuration interaction (CI) method

CI energy

$$E_{\mathrm{CI}} = \min_{\{C_{\mathcal{J}}\}} \frac{\langle \Psi(\{C_{\mathcal{J}}\}) | \hat{H} | \Psi(\{C_{\mathcal{J}}\}) \rangle}{\langle \Psi(\{C_{\mathcal{J}}\}) | \Psi(\{C_{\mathcal{J}}\}) \rangle}$$

CI wave function

$$\Psi(\{C_{\mathcal{J}}\}) = \sum_{\mathcal{J}}^{determinants} C_{\mathcal{J}} | \det_{\mathcal{J}} \rangle$$

Configuration interaction (CI) method

CI energy

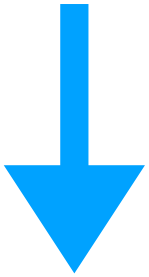
$$E_{\mathrm{CI}} = \min_{\{C_{\mathscr{I}}\}} \frac{\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle}{\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle}$$

The minimising CI coefficients are obtained by
diagonalising the (so-called CI) ***Hamiltonian matrix***

$$\mathbf{H} \equiv \left\{ H_{\mathscr{L}\mathscr{I}} = \langle \det_{\mathscr{L}} | \hat{H} | \det_{\mathscr{I}} \rangle \right\}$$

Proof:

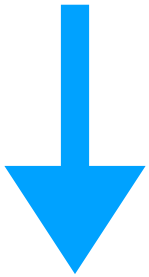
$$E_{\mathrm{CI}} = \min_{\{C_{\mathscr{I}}\}} \frac{\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle}{\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle}$$



$$\frac{\partial}{\partial C_{\mathscr{L}}} \frac{\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle}{\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle} = 0$$

Proof:

$$\frac{\partial}{\partial C_{\mathscr{L}}} \frac{\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle}{\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle} = 0$$



$$\frac{\partial}{\partial C_{\mathscr{L}}} \left[\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle \right]$$

$$= \frac{\partial}{\partial C_{\mathscr{L}}} \left[\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle \times \frac{\langle \Psi(\{C_{\mathscr{I}}\}) | \hat{H} | \Psi(\{C_{\mathscr{I}}\}) \rangle}{\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle} \right]$$

$$= E_{\mathrm{CI}} \times \frac{\partial}{\partial C_{\mathscr{L}}} \left[\langle \Psi(\{C_{\mathscr{I}}\}) | \Psi(\{C_{\mathscr{I}}\}) \rangle \right]$$

Proof:

$$\frac{\partial}{\partial C_{\mathscr{L}}}\left[\langle\Psi(\{C_{\mathscr{J}}\})|\hat{H}|\Psi(\{C_{\mathscr{J}}\})\rangle\right] = E_{\mathrm{CI}}\frac{\partial}{\partial C_{\mathscr{L}}}\left[\langle\Psi(\{C_{\mathscr{J}}\})|\Psi(\{C_{\mathscr{J}}\})\rangle\right]$$

Proof:

$$\frac{\partial}{\partial C_{\mathscr{L}}}\left[\langle\Psi(\{C_{\mathscr{I}}\})|\hat{H}|\Psi(\{C_{\mathscr{I}}\})\rangle\right] = E_{\mathrm{CI}}\frac{\partial}{\partial C_{\mathscr{L}}}\left[\langle\Psi(\{C_{\mathscr{I}}\})|\Psi(\{C_{\mathscr{I}}\})\rangle\right]$$

$$= 2\langle\frac{\partial\Psi(\{C_{\mathscr{I}}\})}{\partial C_{\mathscr{L}}}|\hat{H}|\Psi(\{C_{\mathscr{I}}\})\rangle$$

$$= 2\langle\det{}_{\mathscr{L}}|\hat{H}|\Psi(\{C_{\mathscr{I}}\})\rangle$$

Proof:

$$2\langle \det_{\mathscr{L}} | \hat{H} | \Psi(\{C_{\mathscr{F}}\})\rangle = E_{\mathrm{CI}} \frac{\partial}{\partial C_{\mathscr{L}}} \left[\langle \Psi(\{C_{\mathscr{F}}\}) | \Psi(\{C_{\mathscr{F}}\})\rangle\right]$$

$$2E_{\mathrm{CI}} \times \langle \det_{\mathscr{L}} | \Psi(\{C_{\mathscr{F}}\})\rangle$$

Proof:

$$\langle \det_{\mathcal{L}} | \hat{H} | \Psi(\{C_{\mathcal{I}}\}) \rangle = E_{\mathrm{CI}} \times \langle \det_{\mathcal{L}} | \Psi(\{C_{\mathcal{I}}\}) \rangle$$

$$\Psi(\{C_{\mathcal{I}}\}) = \sum_{\mathcal{I}}^{determinants} C_{\mathcal{I}} | \det_{\mathcal{I}} \rangle$$

$$\sum_{\mathcal{I}} C_{\mathcal{I}} \langle \det_{\mathcal{L}} | \hat{H} | \det_{\mathcal{I}} \rangle$$

$$= \sum_{\mathcal{I}} H_{\mathcal{L}\mathcal{I}} C_{\mathcal{I}}$$

Proof:

$$\sum_{\mathcal{J}} H_{\mathcal{L}\mathcal{J}} C_{\mathcal{J}} = E_{\mathrm{CI}} \times \langle \det_{\mathcal{L}} | \Psi(\{C_{\mathcal{J}}\}) \rangle$$

$$\Psi(\{C_{\mathcal{J}}\}) = \sum_{\mathcal{J}}^{determinants} C_{\mathcal{J}} | \det_{\mathcal{J}} \rangle$$

$$C_{\mathcal{L}}$$

Proof:

$$\sum_{\mathcal{J}} H_{\mathcal{L}\mathcal{J}} C_{\mathcal{J}} = E_{\mathrm{CI}} C_{\mathcal{L}}$$

$$\mathbf{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{\mathcal{J}} \\ \vdots \end{bmatrix}$$

$$\left[\mathbf{HC}\right]_{\mathcal{L}}$$

Proof:

$$\left[\mathbf{HC}\right]_{\mathscr{L}} = E_{\mathrm{CI}}\,\mathbf{C}_{\mathscr{L}}$$

$$\mathbf{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{\mathscr{I}} \\ \vdots \end{bmatrix}$$

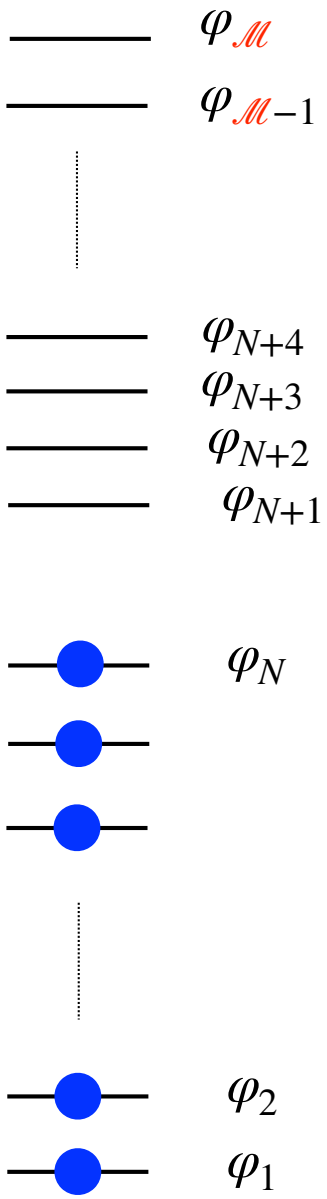
Proof:

$$\left[\mathbf{HC}\right]_{\mathscr{L}} = E_{\mathrm{CI}}\,\mathbf{C}_{\mathscr{L}}$$

$$\mathbf{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{\mathscr{I}} \\ \vdots \end{bmatrix} \quad \Updownarrow$$

$$\mathbf{HC} = E_{\mathrm{CI}}\,\mathbf{C}$$

How many determinants in total?



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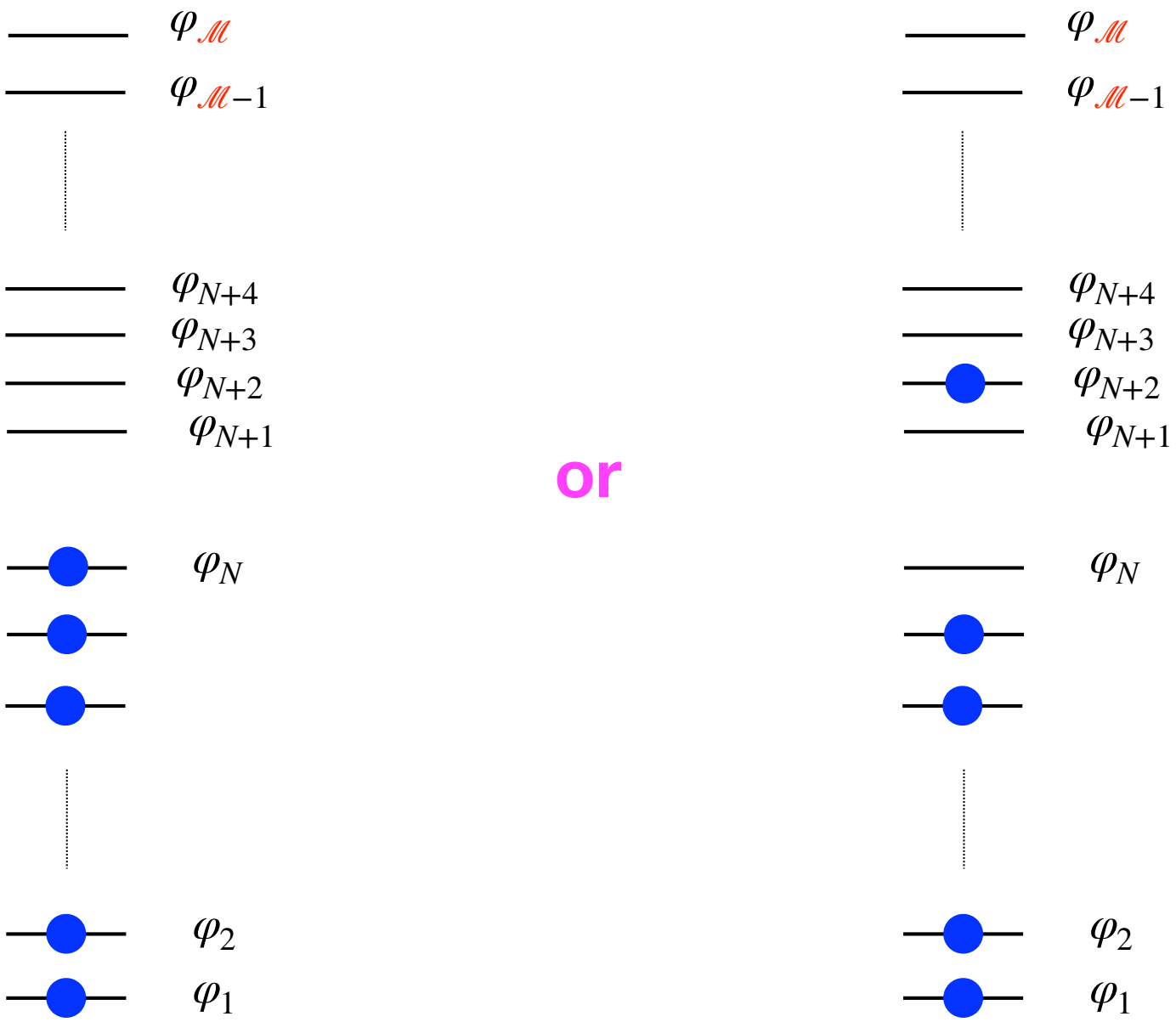

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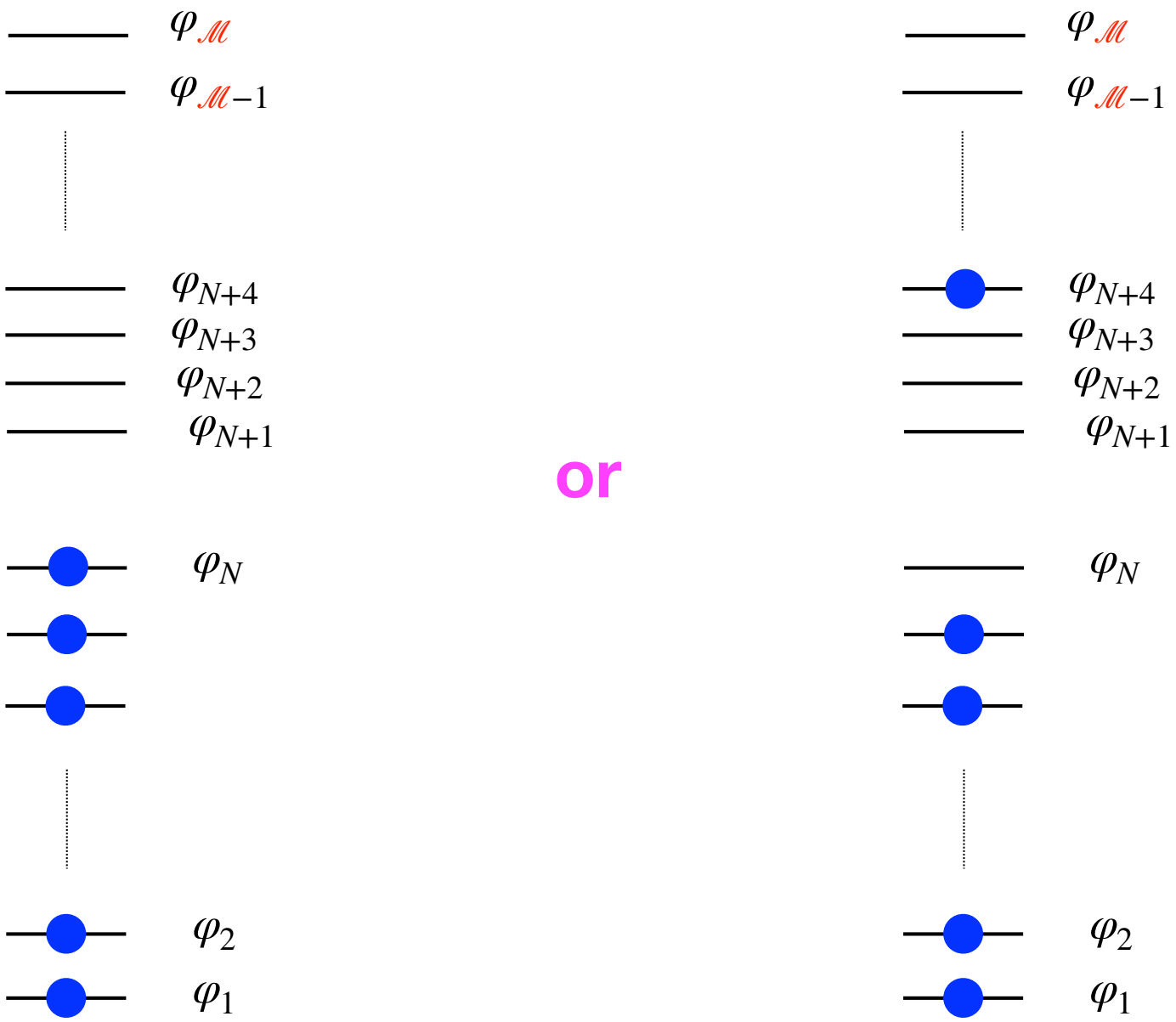

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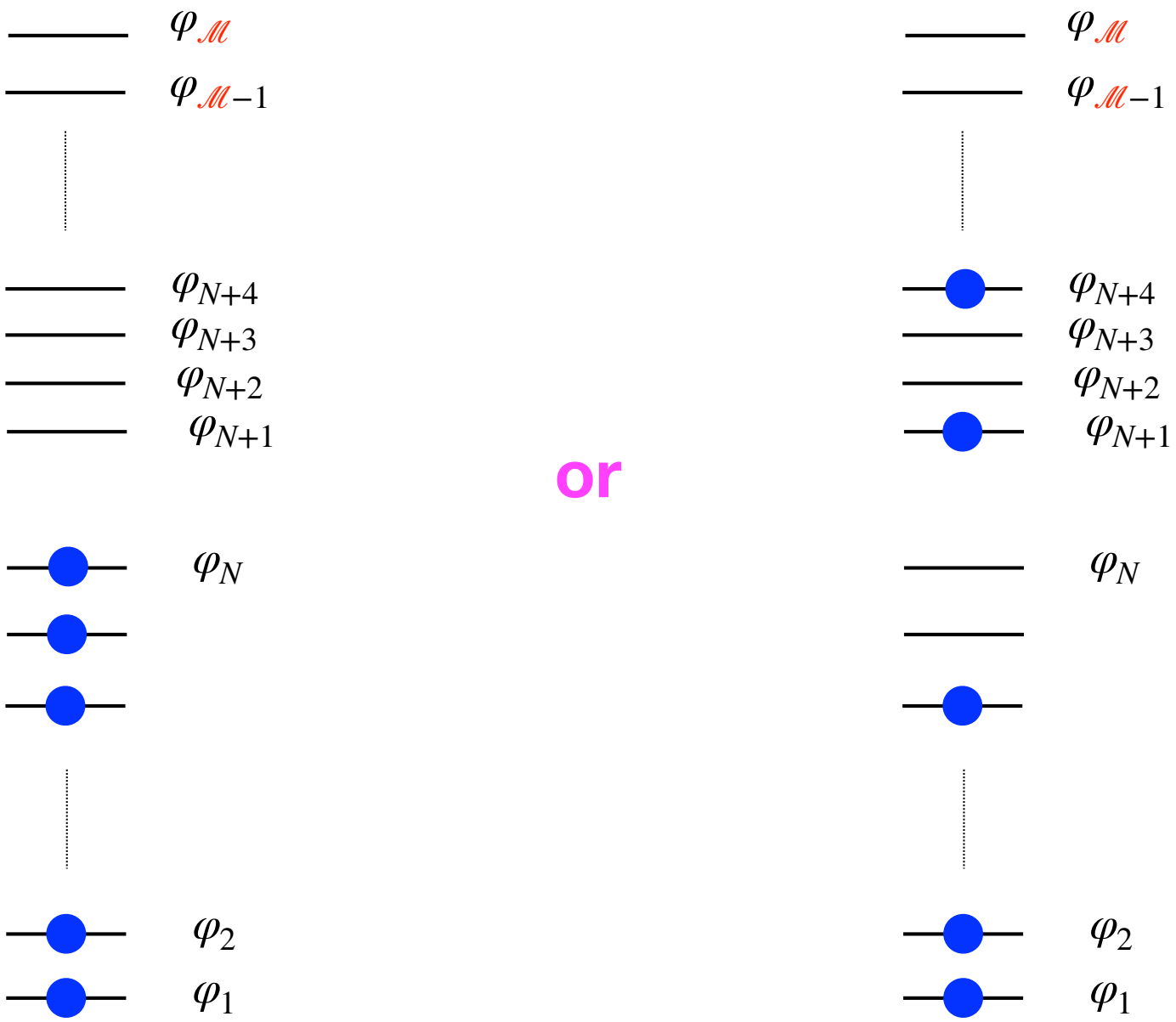
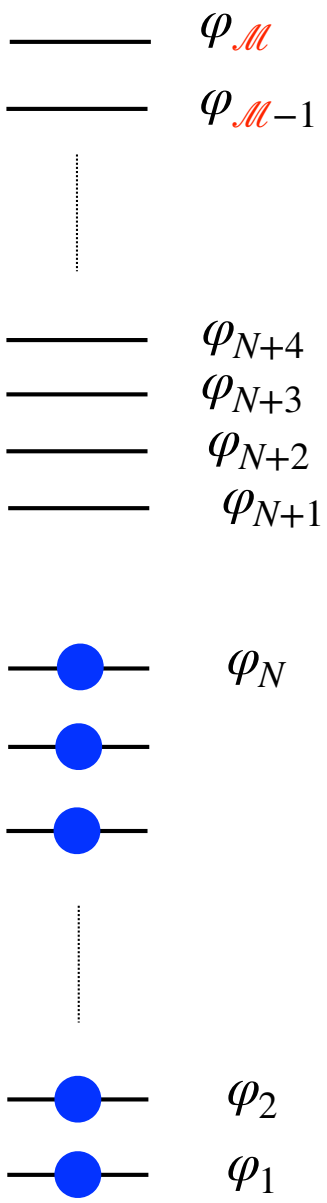
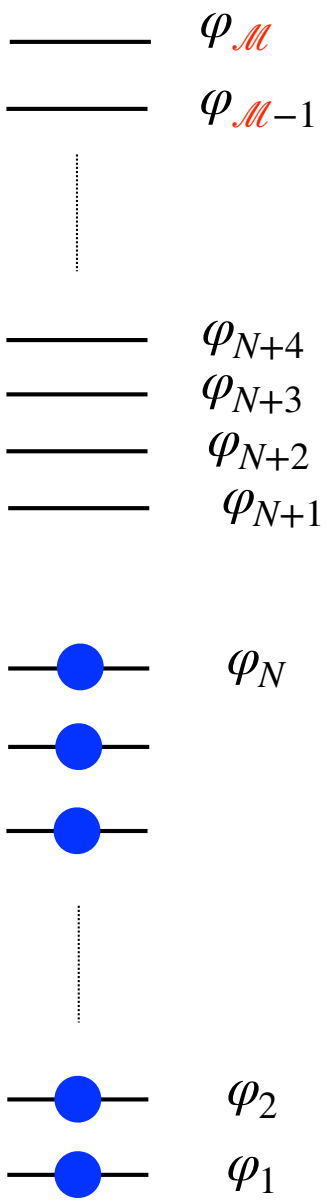


How many determinants in total?



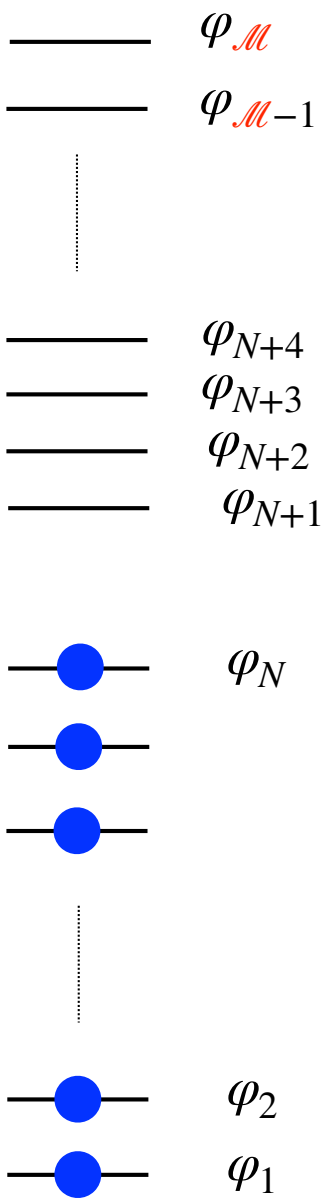
or *Etc…*

How many determinants in total?



We have $\mathscr{M}$ spin-orbitals available for N electrons

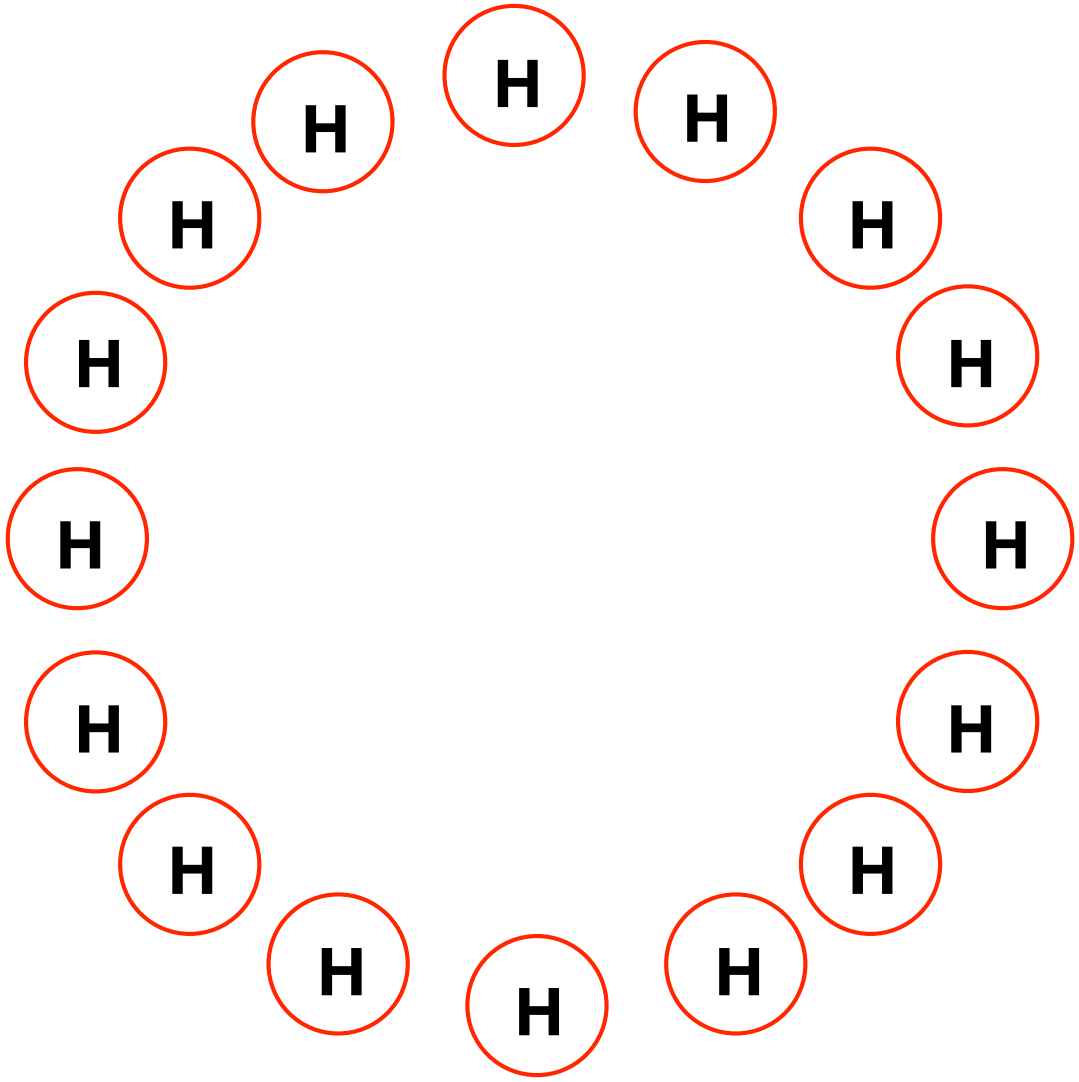
How many determinants in total?



We have $\mathscr{M}$ spin-orbitals available for N electrons

$$N_{\text{det.}} = \binom{\mathscr{M}}{N} = \frac{\mathscr{M}!}{N!(\mathscr{M}-N)!}$$

How many determinants in total?



$$\mathscr{M} = 2 \times N$$

Spin

How many determinants in total?

$$\mathscr{M} = 2 \times N$$

$$N_{\text{det.}} = \frac{\mathscr{M}!}{N!(\mathscr{M}-N)!} = \frac{(2N)!}{(N!)^2}$$

How many determinants in total?

$$\mathscr{M} = 2 \times N$$

$$N_{\text{det.}} = \frac{\mathscr{M}!}{N!(\mathscr{M}-N)!} = \frac{(2N)!}{(N!)^2}$$

$$N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

Stirling formula for large N values

$$\approx \frac{2^{2N}}{\sqrt{\pi N}} = \frac{e^{2N \ln 2}}{\sqrt{\pi N}}$$

How many determinants in total?

$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}}$$

"Exponential wall"

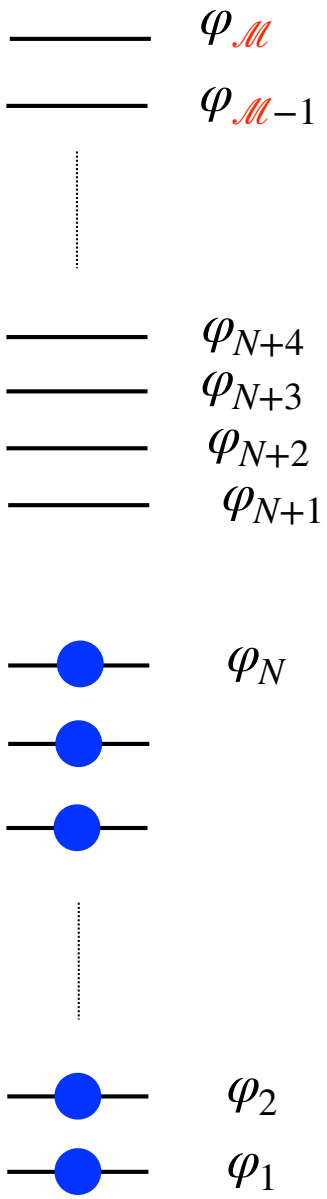
How many determinants in total?

$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=50}{\approx} 10^{29}$$

How many determinants in total?

$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=400}{\approx} 1.88 \times 10^{239}$$

Complete active space CI (CAS-CI) method



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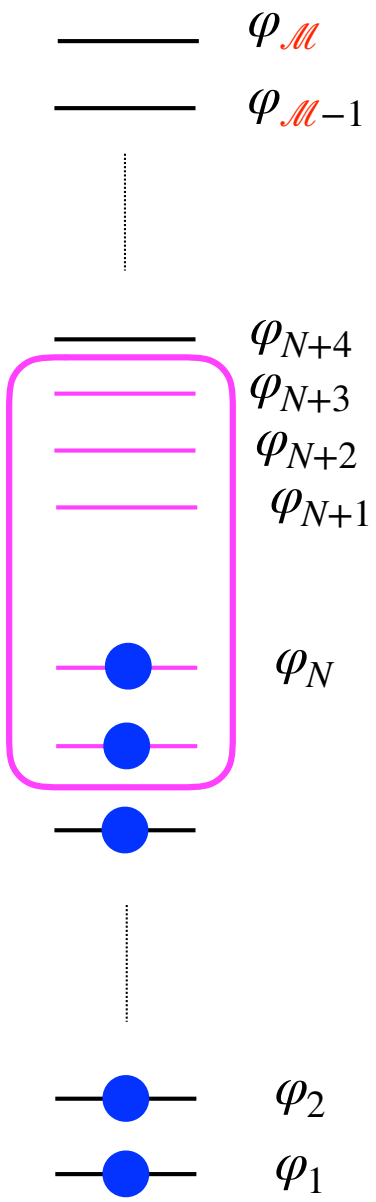

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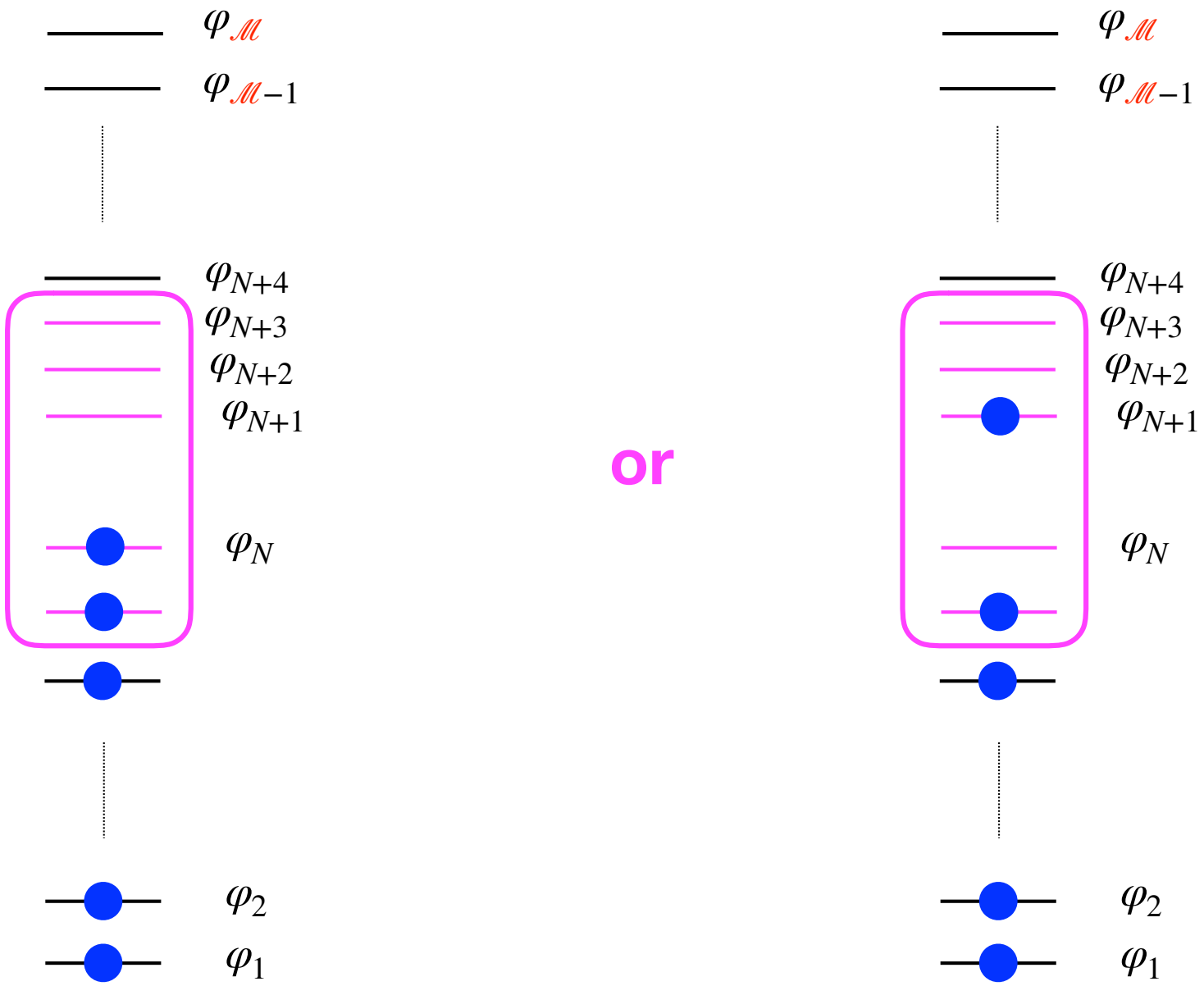
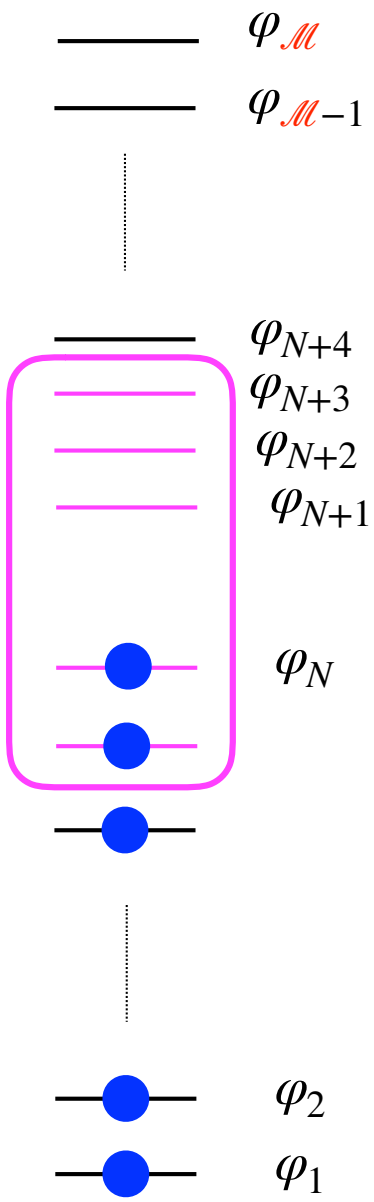
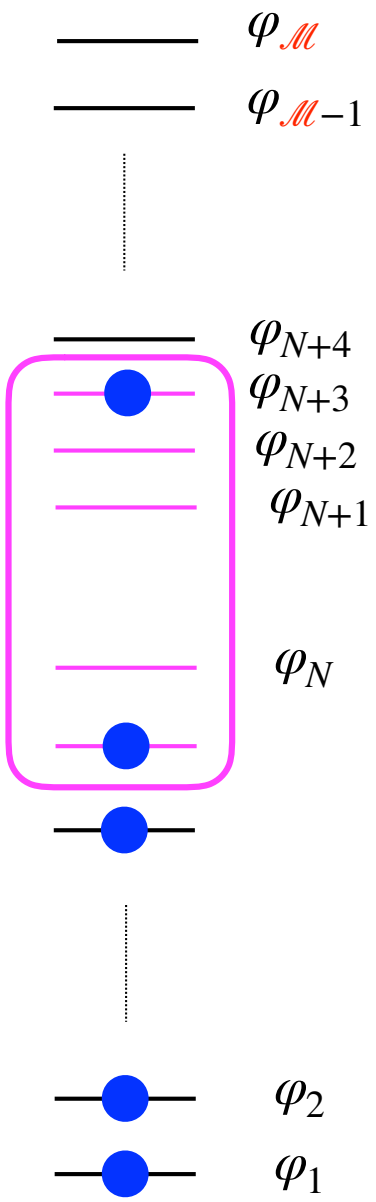


Complete active space CI (CAS-CI) method



or



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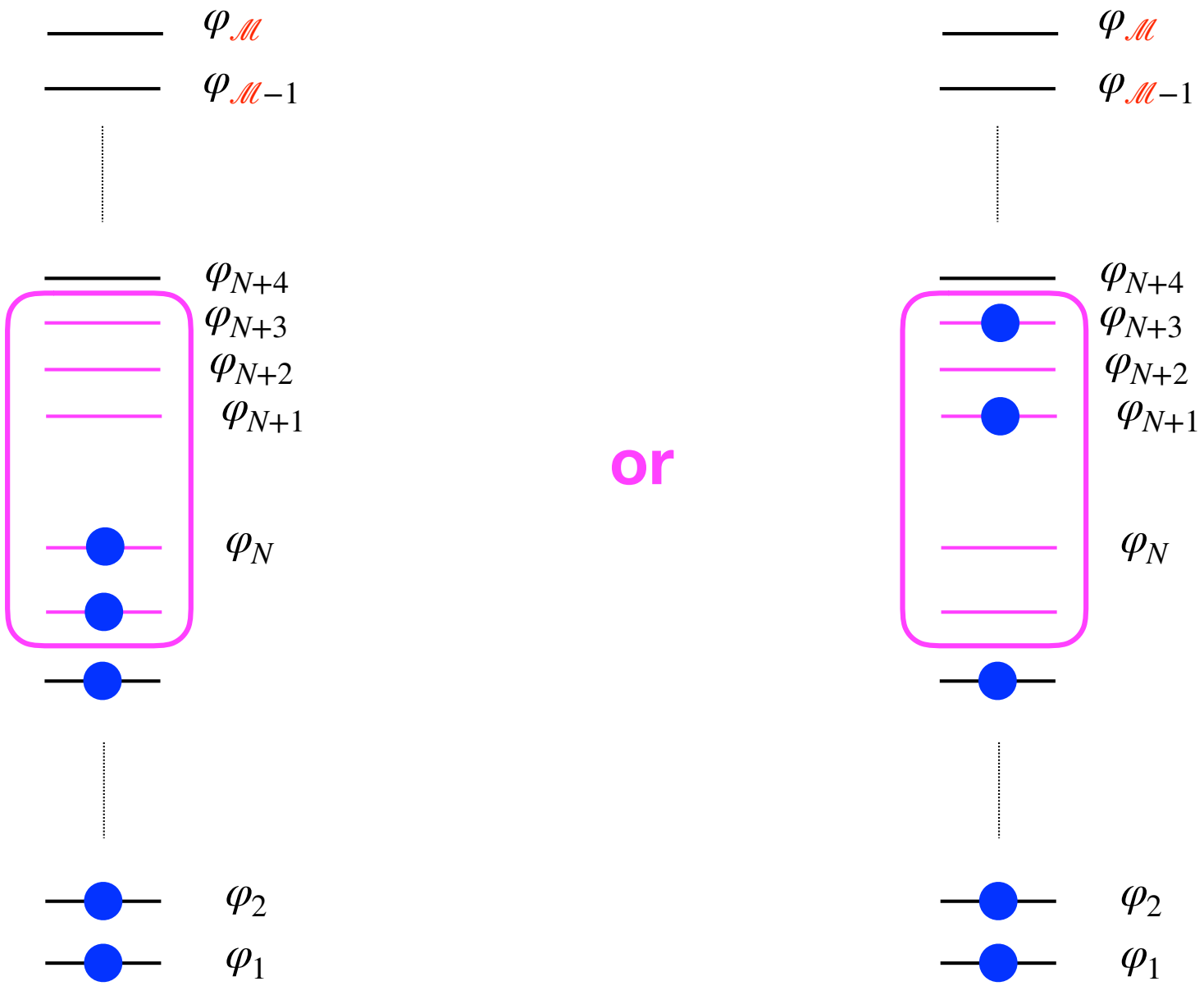
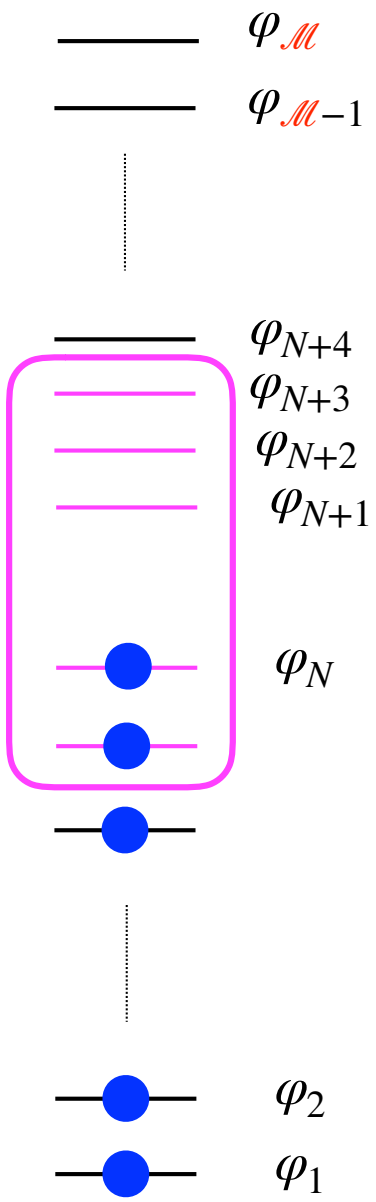
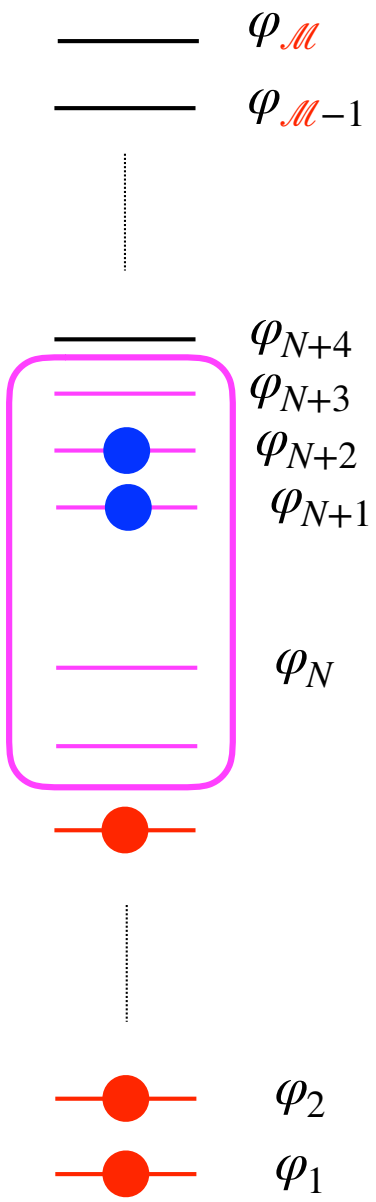


Complete active space CI (CAS-CI) method



or *Etc…*

Complete active space CI (CAS-CI) method



Active *orbitals*

Inactive core orbitals

Projection operators in the N-electron space

$$|\Psi\rangle = \sum_{\mathcal{I}}^{determinants} C_{\mathcal{I}} |\det_{\mathcal{I}}\rangle$$

Projection operators in the N-electron space

$$|\Psi\rangle = \sum_{\mathscr{I}}^{determinants} C_{\mathscr{I}} |\det_{\mathscr{I}}\rangle$$

$$\langle \det_{\mathscr{L}} | \Psi \rangle = C_{\mathscr{L}}$$

Projection operators in the N-electron space

$$|\Psi\rangle = \sum_{\mathcal{I}}^{determinants} C_{\mathcal{I}} |\det_{\mathcal{I}}\rangle$$

$$\langle \det_{\mathcal{L}} | \Psi \rangle = C_{\mathcal{L}}$$

$$\sum_{\mathcal{L}}^{determinants} |\det_{\mathcal{L}}\rangle\langle \det_{\mathcal{L}} | \Psi \rangle = |\Psi\rangle$$

Projection operators in the N-electron space

$$\sum_{\mathscr{L}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1} \longleftarrow \text{Identity operator} \left(\hat{1}\,|\Psi\rangle = |\Psi\rangle\right)$$

$$\sum_{\mathscr{L}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}|\Psi\rangle = |\Psi\rangle$$

Projection operators in the N-electron space

$$\sum_{\mathscr{L}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

"resolution of the identity"

Projection operators in the N-electron space

$$\sum_{\mathscr{L}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

"resolution of the identity"

$$\Updownarrow$$

$$\sum_{\mathscr{L}\in \mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| + \sum_{\mathscr{L}\notin \mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

Projection operators in the N-electron space

Partitioning** of the N-electron space into **two subspaces

$$\sum_{\mathscr{L}\in\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| + \sum_{\mathscr{L}\notin\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

Projection operators in the N-electron space

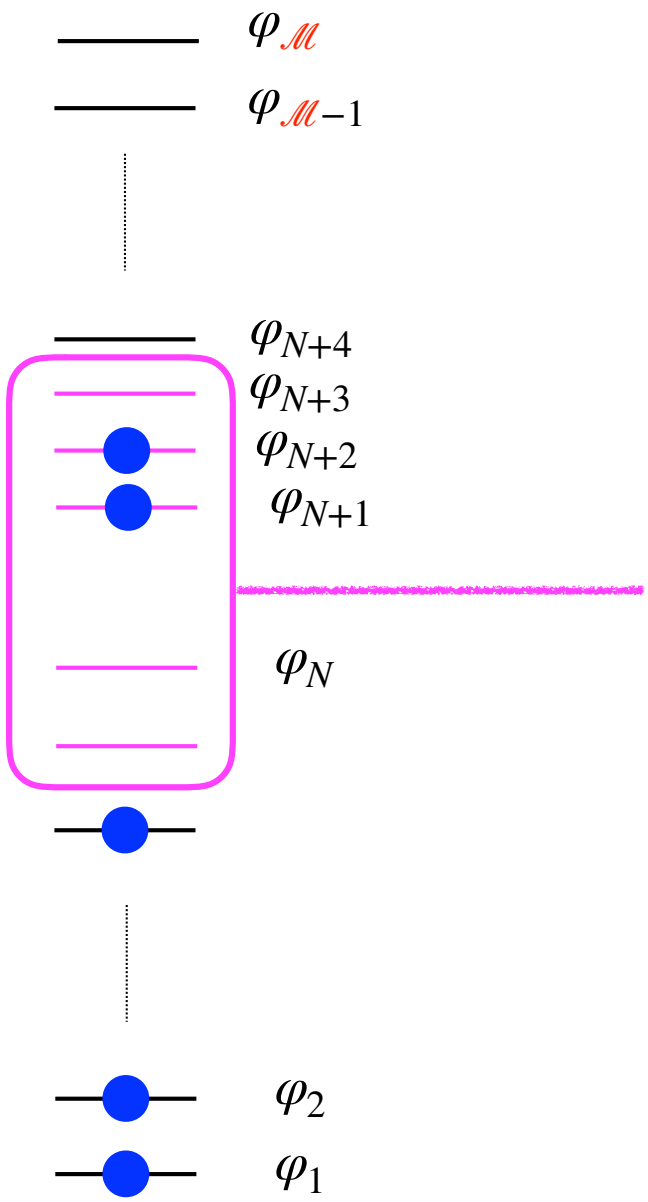
To-be-embedded subspace

$$\sum_{\mathscr{L}\in\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| + \sum_{\mathscr{L}\notin\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

Projection operators in the N-electron space

$$\underbrace{\sum_{\mathscr{L}\in\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}|}_{\hat{P}} + \sum_{\mathscr{L}\notin\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}| \equiv \hat{1}$$

Complete active space (CAS) and effective Hamiltonian



$$\hat{P} = \sum_{\mathscr{L} \in \mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}|$$

Projection operators in the N-electron space

$$\overbrace{\sum_{\mathscr{L}\in\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}|}^{\hat{P}} + \overbrace{\sum_{\mathscr{L}\notin\mathrm{CAS}}^{determinants} |\det_{\mathscr{L}}\rangle\langle\det_{\mathscr{L}}|}^{\hat{Q}} \equiv \hat{1}$$

Effective Hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

Effective Hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = \left(\hat{P}+\hat{Q}\right)|\Psi\rangle = \hat{P}|\Psi\rangle + \hat{Q}|\Psi\rangle$$

Effective Hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = \left(\hat{P}+\hat{Q}\right)|\Psi\rangle = \boxed{\hat{P}|\Psi\rangle} + \hat{Q}|\Psi\rangle$$

To-be-embedded *part of the N-electron wave function*

Effective Hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = \left(\hat{P}+\hat{Q}\right)|\Psi\rangle = \hat{P}|\Psi\rangle + \hat{Q}|\Psi\rangle$$

Can be determined from $\hat{P}|\Psi\rangle$

Proof:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{Q}\hat{H}|\Psi\rangle = E\hat{Q}|\Psi\rangle$$

$$\hat{Q}\hat{H}\left(\hat{P}+\hat{Q}\right)|\Psi\rangle = E\hat{Q}|\Psi\rangle$$

$$\hat{Q}\hat{H}\hat{P}|\Psi\rangle + \hat{Q}\hat{H}\hat{Q}|\Psi\rangle = E\hat{Q}|\Psi\rangle$$

$$\hat{Q}\hat{H}\hat{P}|\Psi\rangle = \left(E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right)\hat{Q}|\Psi\rangle \qquad \hat{Q}^2 = \hat{Q}$$

$$\hat{Q}|\Psi\rangle = \left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}|\Psi\rangle$$

Effective Hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{P}\hat{H}|\Psi\rangle = E\hat{P}|\Psi\rangle$$

$$\hat{P}\hat{H}\left(\hat{P}+\hat{Q}\right)|\Psi\rangle = E\hat{P}|\Psi\rangle$$

$$\hat{P}\hat{H}\hat{P}|\Psi\rangle+\hat{P}\hat{H}\hat{Q}|\Psi\rangle = E\hat{P}|\Psi\rangle$$

$$\hat{P}\hat{H}\hat{P}|\Psi\rangle+\hat{P}\hat{H}\left[E\hat{Q}-\hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}|\Psi\rangle = E\hat{P}|\Psi\rangle$$

$$\hat{H}_{\text{eff}}(E)\hat{P}|\Psi\rangle = E\hat{P}|\Psi\rangle$$

Effective Hamiltonian

$$\hat{H}_{\text{eff}}(E)\hat{P}\,|\Psi\rangle = E\,\hat{P}\,|\Psi\rangle$$

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}$$

Effective Hamiltonian

$$\hat{H}_{\text{eff}}(E)\hat{P}\,|\Psi\rangle = E\hat{P}\,|\Psi\rangle$$

Embedded wave function

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}$$

Effective Hamiltonian

$$\hat{H}_{\text{eff}}(E)\hat{P}\,|\Psi\rangle = E\,\hat{P}\,|\Psi\rangle$$

"Embedding Hamiltonian"

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}$$

Effective Hamiltonian

$$\hat{H}_{\text{eff}}(E)\hat{P}\,|\Psi\rangle = E\,\hat{P}\,|\Psi\rangle$$

Energy *(i.e frequency- or time-)* ***dependent***

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}$$

Analogy with the Green's function formalism

$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\underbrace{\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}}_{\hat{R}(E)}\hat{Q}\hat{H}\hat{P}$$

Resolvent operator

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

Full Hamiltonian

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

Full Hamiltonian

Difficult to solve…

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

Full Hamiltonian

Perturbative approach:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

Easier to solve *"unperturbed" Hamiltonian (usually one-electron)*

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

Full Hamiltonian

Perturbative approach:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

Fock operator *in Moeller-Plesset second-order perturbation theory (MP2)*

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

Full Hamiltonian

Perturbative approach:

$$\hat{H} = \hat{H}_0 + \hat{V}$$

"perturbation"

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}\hat{Q}$$

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}_0\hat{Q} - \hat{Q}\hat{V}\hat{Q}$$

Analogy with the Green's function formalism

$$\left[\hat{R}_0(E)\right]^{-1}$$

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}_0\hat{Q} - \hat{Q}\hat{V}\hat{Q}$$

Inverse of the
unperturbed *resolvent*

Analogy with the Green's function formalism

$$\left[\hat{R}_0(E)\right]^{-1} \qquad \hat{\Sigma}$$

$$\left[\hat{R}(E)\right]^{-1} = E\hat{Q} - \hat{Q}\hat{H}_0\hat{Q} - \hat{Q}\hat{V}\hat{Q}$$

analog** of the **self-energy
(energy-independent here)

Analogy with the Green's function formalism

$$\left[\hat{R}(E)\right]^{-1} = \left[\hat{R}_0(E)\right]^{-1} - \hat{\Sigma}$$

Analogy with the Green's function formalism

$$\hat{R}_0(E)\times \longrightarrow \left[\hat{R}(E)\right]^{-1} = \left[\hat{R}_0(E)\right]^{-1} - \hat{\Sigma} \longleftarrow \times \hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}_0(E)\times \longrightarrow \left[\hat{R}(E)\right]^{-1} = \left[\hat{R}_0(E)\right]^{-1} - \hat{\Sigma} \longleftarrow \times \hat{R}(E)$$

$$\downarrow$$

$$\hat{R}_0(E)\left[\hat{R}(E)\right]^{-1}\hat{R}(E) = \hat{R}_0(E)\left[\hat{R}_0(E)\right]^{-1}\hat{R}(E) - \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}_0(E)\times \longrightarrow \left[\hat{R}(E)\right]^{-1} = \left[\hat{R}_0(E)\right]^{-1} - \hat{\Sigma} \longleftarrow \times \hat{R}(E)$$

$$\downarrow$$

$$\hat{R}_0(E)\left[\hat{R}(E)\right]^{-1}\hat{R}(E) = \hat{R}_0(E)\left[\hat{R}_0(E)\right]^{-1}\hat{R}(E) - \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$\downarrow$$

$$\hat{R}_0(E) = \hat{R}(E) - \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}_0(E)\times \longrightarrow \left[\hat{R}(E)\right]^{-1} = \left[\hat{R}_0(E)\right]^{-1} - \hat{\Sigma} \longleftarrow \times \hat{R}(E)$$

$$\hat{R}_0(E)\left[\hat{R}(E)\right]^{-1}\hat{R}(E) = \hat{R}_0(E)\left[\hat{R}_0(E)\right]^{-1}\hat{R}(E) - \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$\hat{R}_0(E) = \hat{R}(E) - \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

One-electron Green function: $\mathbf{G}(E) \equiv \left\{ G_{IJ}(E) \right\}$

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

One-electron Green function: $\mathbf{G}(E) \equiv \left\{ G_{IJ}(E) \right\}$

See the last slides of my online lecture on second quantization*

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

*https://quantique.u-strasbg.fr/lib/exe/fetch.php?media=en:pageperso:ef:istpc2021_second_quantization.pdf

Analogy with the Green's function formalism

One-electron Green function: $\mathbf{G}(E) \equiv \{G_{IJ}(E)\}$

Spin-orbital indices

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

One-electron Green function: $\mathbf{G}(E) \longleftarrow \hat{H}$

Unperturbed Green function: $\mathbf{G}_0(E) \longleftarrow \hat{H}_0$

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

One-electron Green function: $\mathbf{G}(E) \longleftarrow \hat{H}$

Unperturbed Green function: $\mathbf{G}_0(E) \longleftarrow \hat{H}_0$

Dyson equation:

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\boldsymbol{\Sigma}(E)\mathbf{G}(E)$$

*Analog of the **Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

Energy-dependent ***self-energy***

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\boldsymbol{\Sigma}(E)\mathbf{G}(E)$$

Analog of the ***Dyson equation***

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\left(\hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)\right)$$

Analogy with the Green's function formalism

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\left(\hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)\right)$$

$$= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}_0(E) + \left(\hat{R}_0(E)\hat{\Sigma}\right)^2 \hat{R}(E)$$

Analogy with the Green's function formalism

$$\hat{R}(E) = \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)$$

$$= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\left(\hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}(E)\right)$$

$$= \hat{R}_0(E) + \hat{R}_0(E)\hat{\Sigma}\hat{R}_0(E) + \left(\hat{R}_0(E)\hat{\Sigma}\right)^2 \hat{R}(E)$$

$$= \hat{R}_0(E) + \sum_{p=1}^{+\infty} \left(\hat{R}_0(E)\hat{\Sigma}\right)^p \hat{R}_0(E)$$

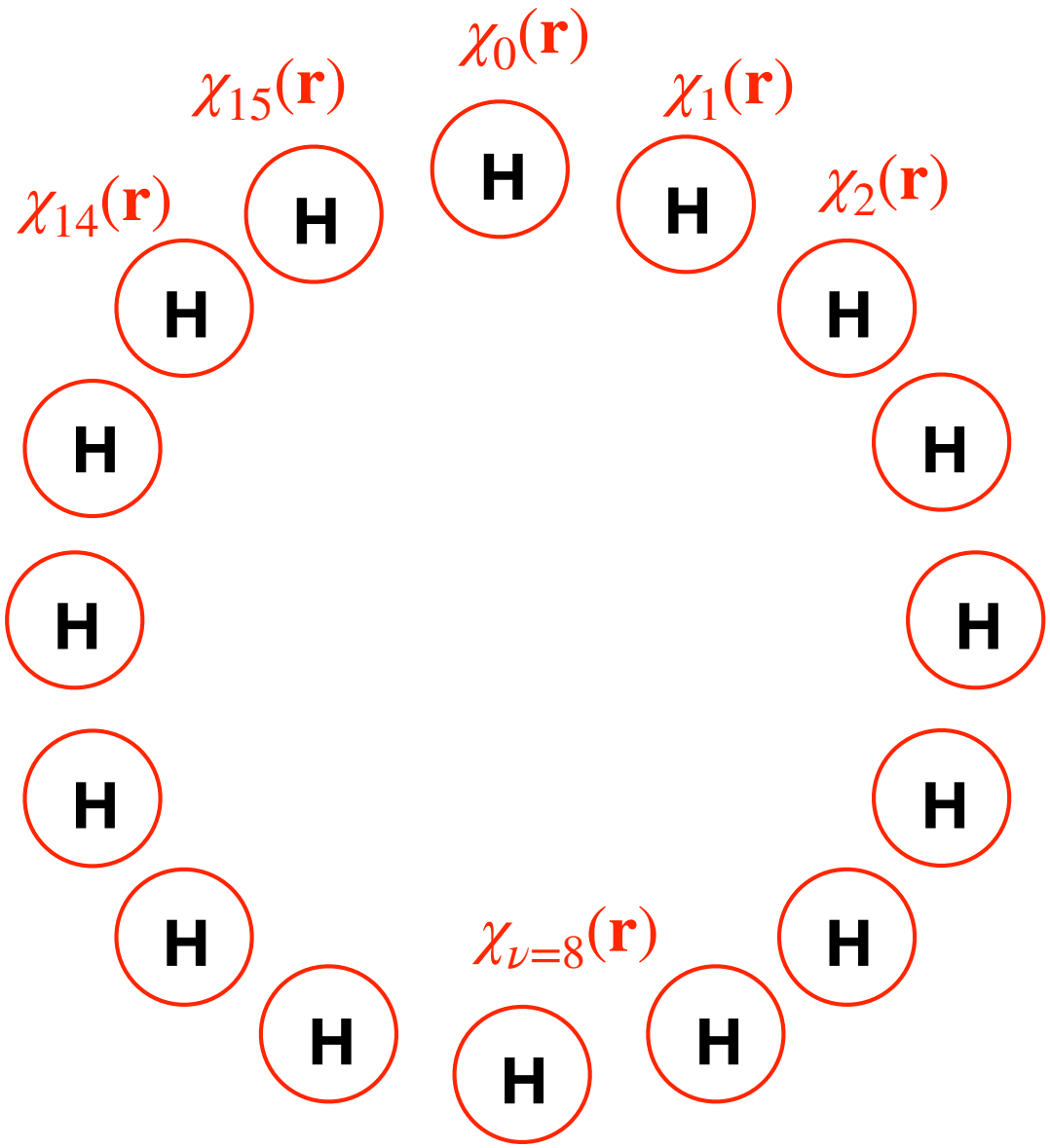
*Infinite-order **perturbation expansion** in* $\hat{\Sigma}$

Strategy 3: Quantum embedding of localized orbitals

Strategy 3: Quantum embedding of localized orbitals

*In this third approach we will proceed with a **fragmentation** of the **electronic Hamiltonian** (written in a **localised** orbital basis) and the design of embedding orbitals*

Prototypical ring of $L = 16$ hydrogen atoms

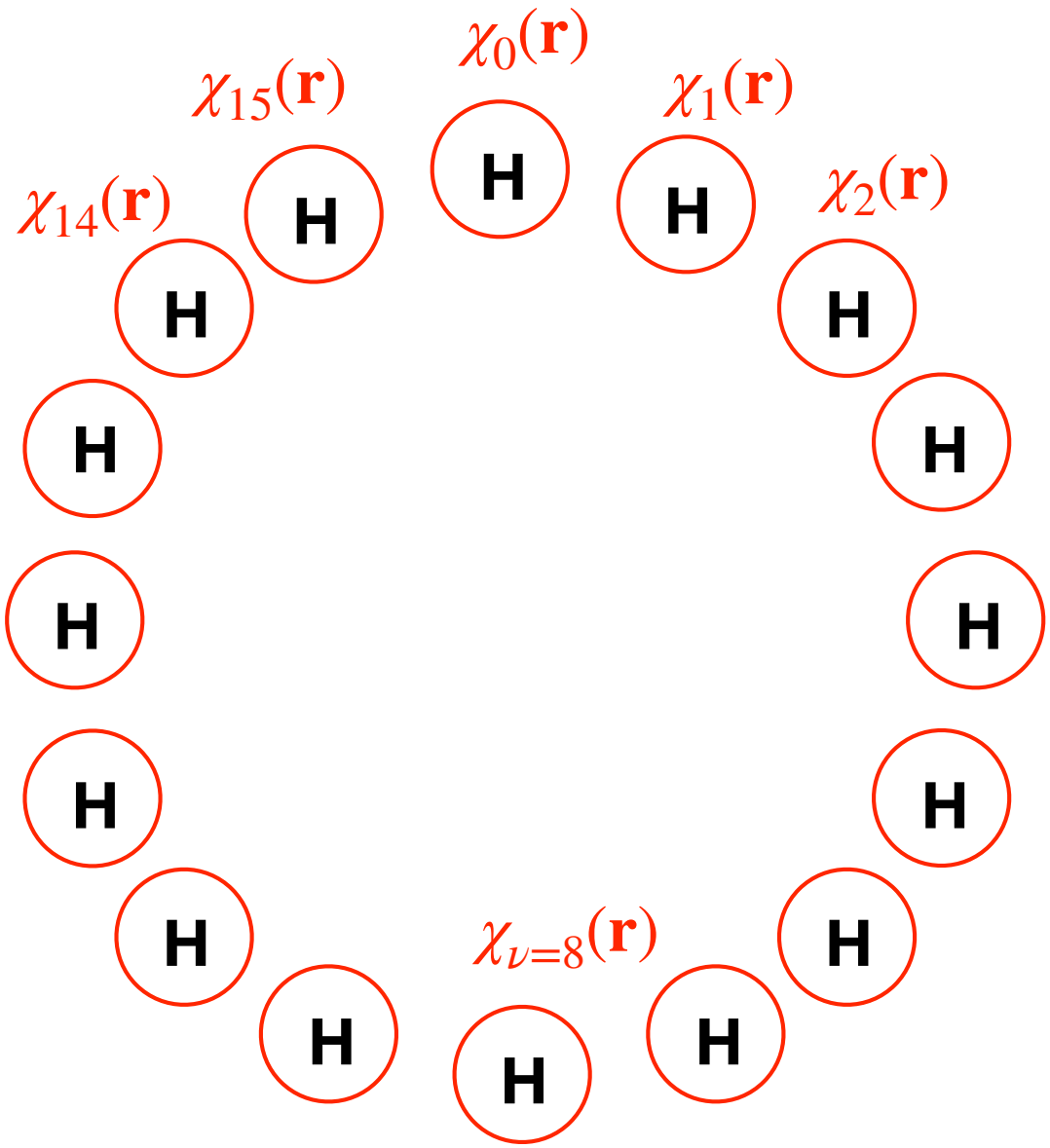


Molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_{\nu} C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Delocalised over the ring

Prototypical ring of $L = 16$ hydrogen atoms



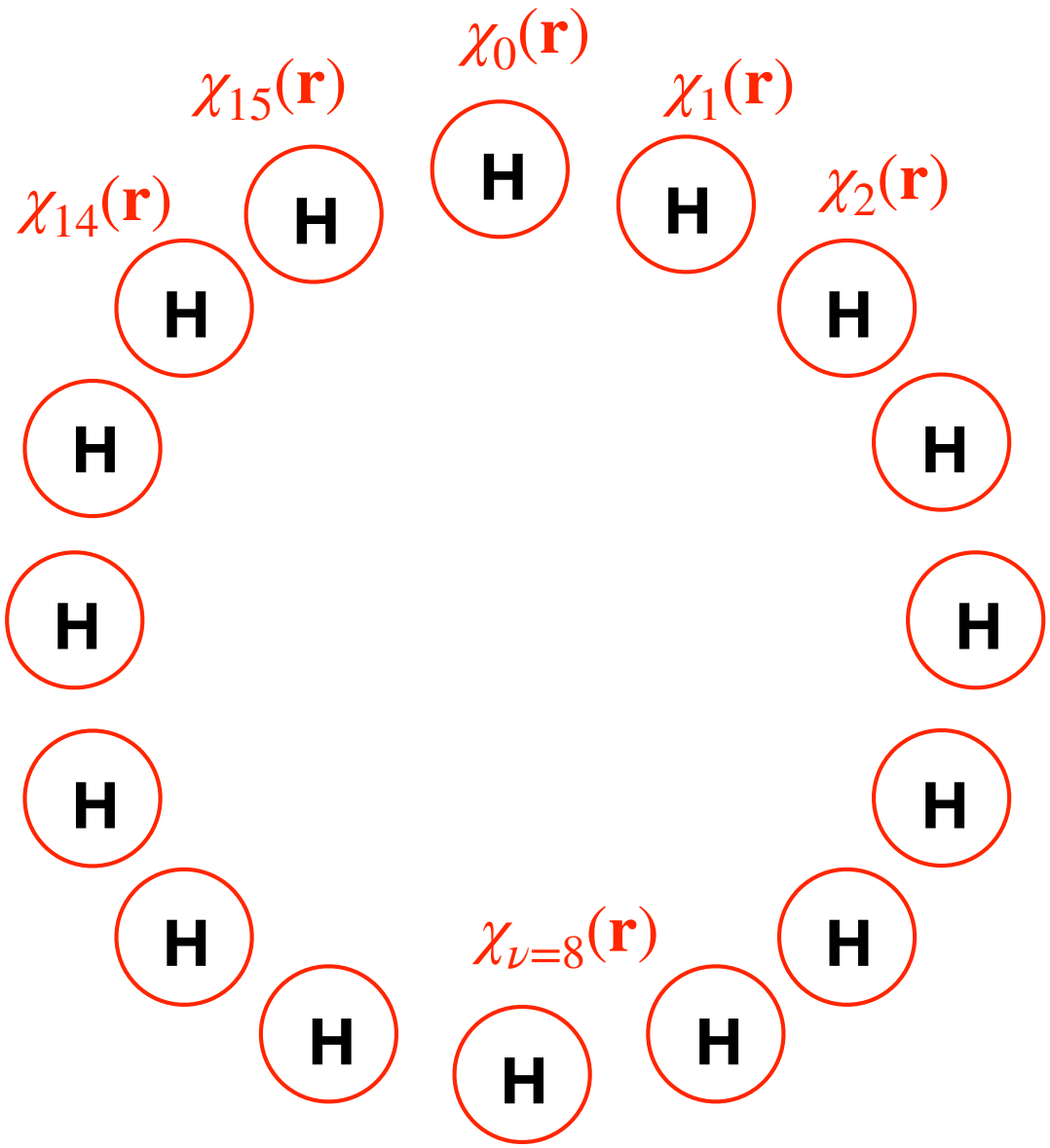
Delocalized molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_\nu C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Dirac notation

$$|\varphi_P\rangle = \sum_\nu C_{\nu P}\, |\chi_\nu\rangle$$

Prototypical ring of $L = 16$ hydrogen atoms



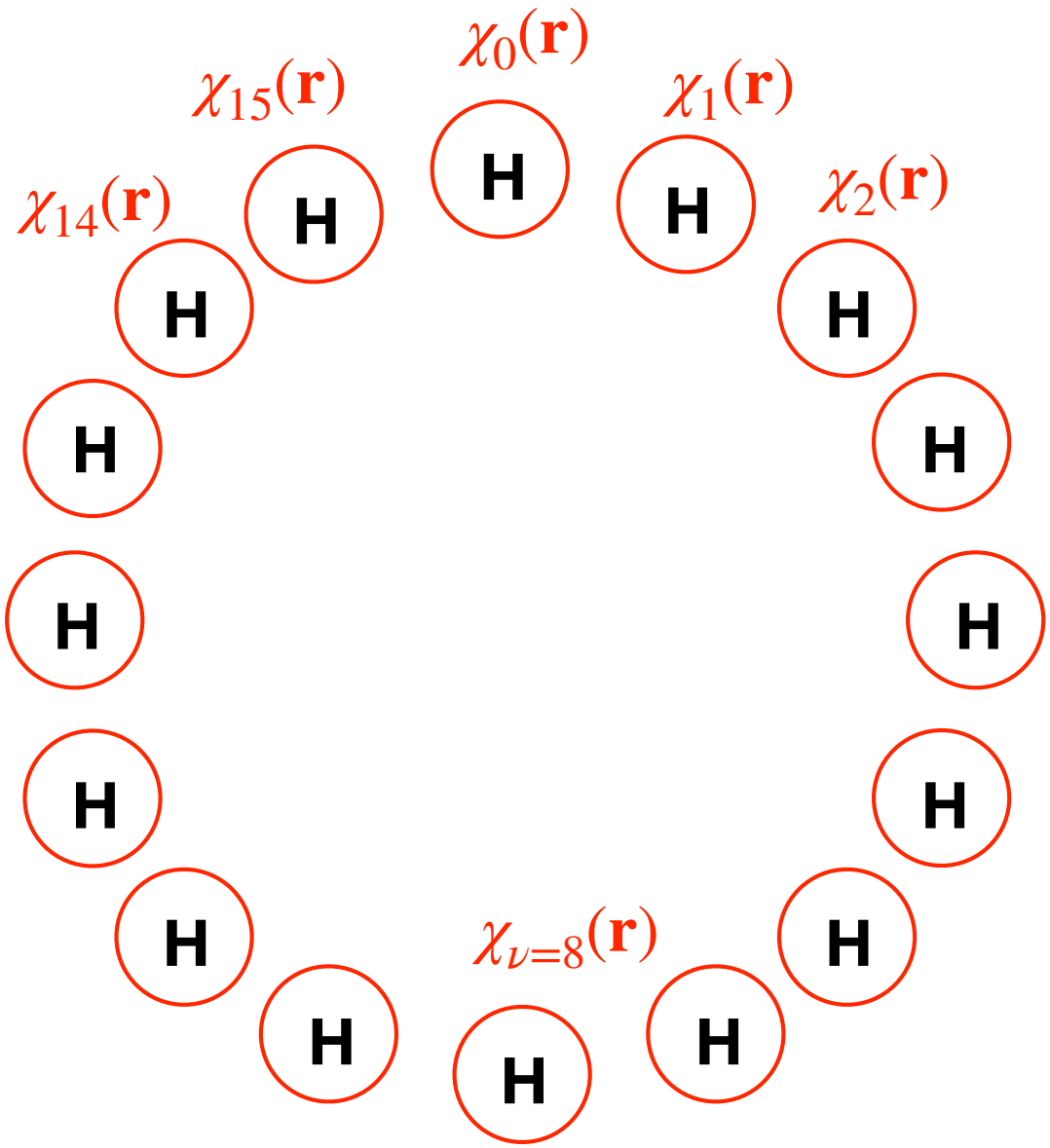
Delocalized molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_\nu C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Second-quantized notation

$$\hat{a}_P^\dagger |\,\mathrm{vac}\rangle = \sum_\nu C_{\nu P}\, \hat{c}_\nu^\dagger |\,\mathrm{vac}\rangle$$

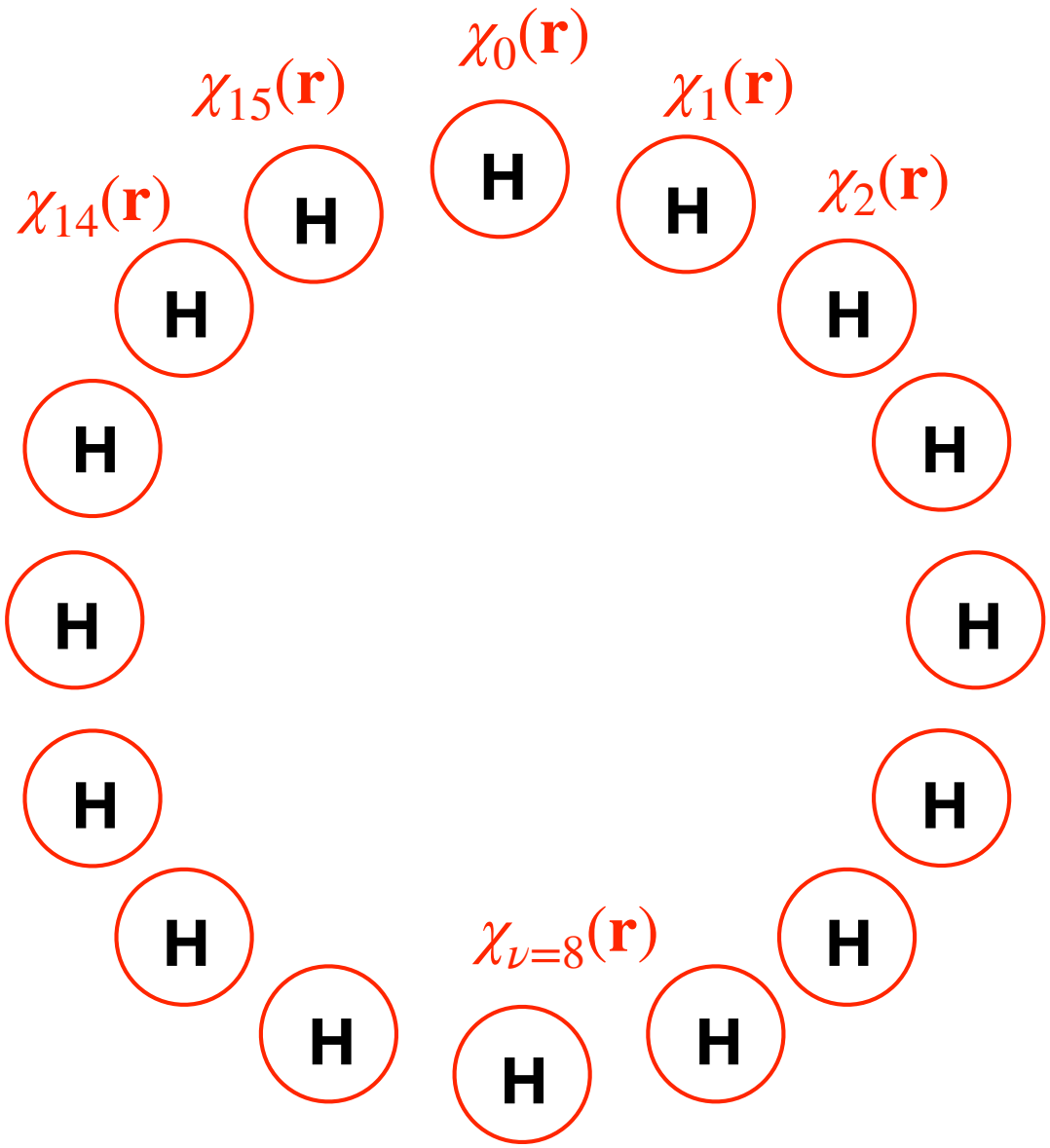
Prototypical ring of $L = 16$ hydrogen atoms



*Creates an electron that occupies the **localised** spin-orbital χ_ν*

$$\hat{a}_P^\dagger |\,\mathrm{vac}\rangle = \sum_\nu C_{\nu P}\, \hat{c}_\nu^\dagger |\,\mathrm{vac}\rangle$$

Prototypical ring of $L = 16$ hydrogen atoms



Delocalized molecular spin-orbitals

$$\varphi_P(\mathbf{x}) = \sum_\nu C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Second-quantized notation

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P}\, \hat{c}_\nu^\dagger$$

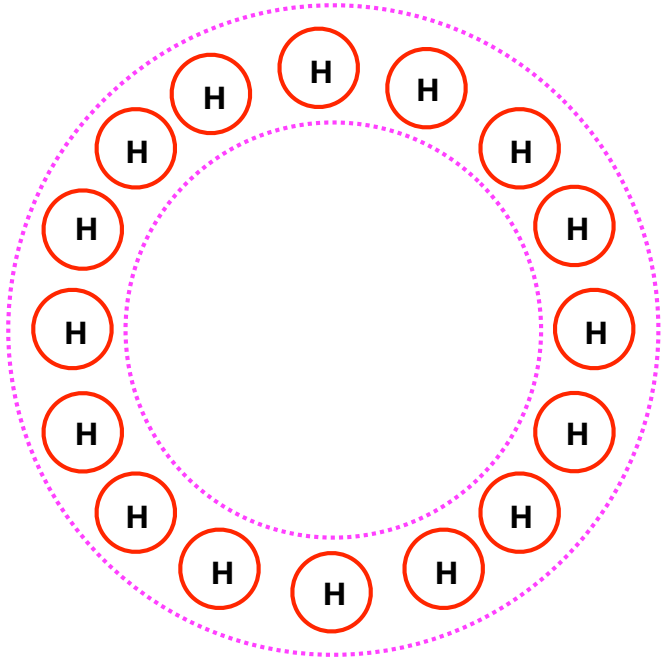
Change of representation in second quantization

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P}\, \hat{c}_\nu^\dagger$$

Change of representation in second quantization

*Chemist's **delocalized** representation*

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P}\, \hat{c}_\nu^\dagger$$

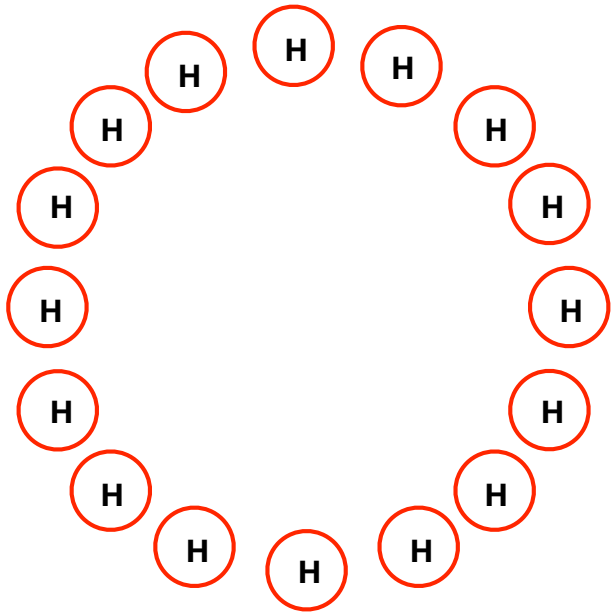


$$\varphi_P(\mathbf{x}) = \sum_\nu C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Change of representation in second quantization

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P} \hat{c}_\nu^\dagger$$

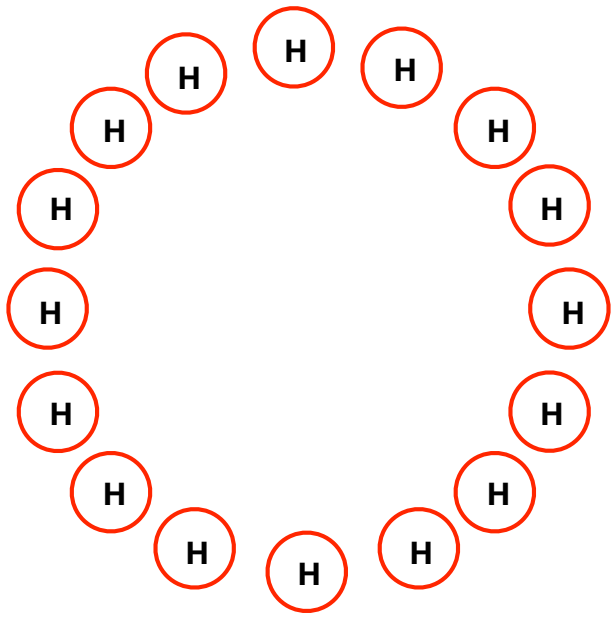
→ *Physicist's **localized** representation*



Change of representation in second quantization

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P} \hat{c}_\nu^\dagger$$

*Physicist's **localized** representation*

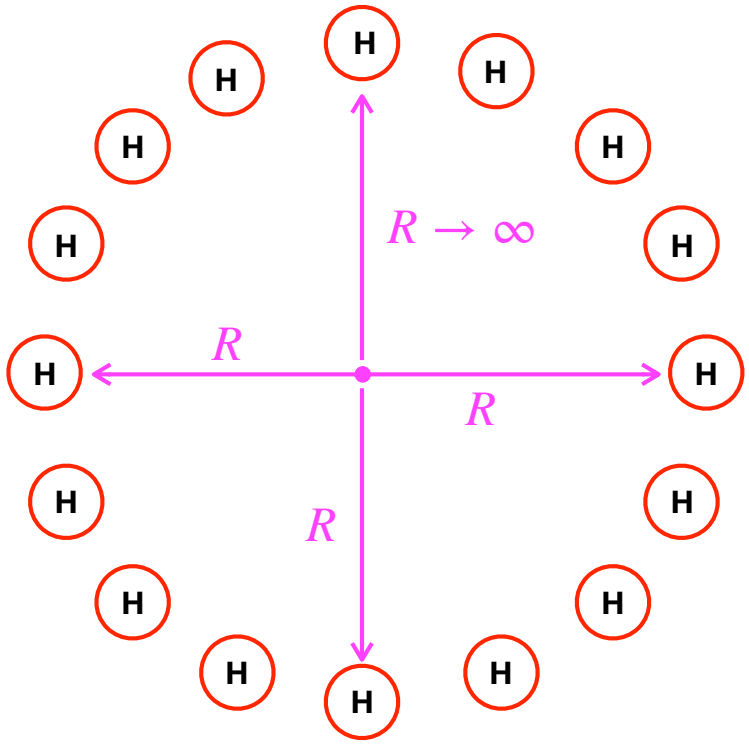


*Allows for a **fragmentation** of the molecule in the orbital space!*

Change of representation in second quantization

$$\hat{a}_P^\dagger = \sum_\nu C_{\nu P} \hat{c}_\nu^\dagger$$

*Physicist's **localized** representation*



*Allows for a **fragmentation** of the molecule in the orbital space!*

*This is a relevant strategy for describing **strong** (local) **electron correlation** effects.*

Hamiltonian in the localised representation

Delocalized *representation*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Hamiltonian in the localised representation

Delocalized *representation*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\hat{a}_P^\dagger = \sum_\mu C_{\mu P} \hat{c}_\mu^\dagger$$

Hamiltonian in the localised representation

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$$\hat{a}_P^\dagger = \sum_\mu C_{\mu P} \hat{c}_\mu^\dagger \qquad \hat{a}_Q = \sum_\nu C_{\nu Q} \hat{c}_\nu$$

Hamiltonian in the localised representation

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$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \, \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\hat{a}_P^\dagger = \sum_{\mu} C_{\mu P} \, \hat{c}_\mu^\dagger \qquad \hat{a}_Q = \sum_{\nu} C_{\nu Q} \, \hat{c}_\nu$$

$$\sum_{\mu\nu} \underbrace{\left(\sum_{PQ} C_{\mu P} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, C_{\nu Q} \right)}_{\overline{h}_{\mu\nu}} \hat{c}_\mu^\dagger \hat{c}_\nu$$

Hamiltonian in the localised representation

Delocalized *representation*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \, \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\hat{a}_P^\dagger = \sum_{\mu} C_{\mu P} \, \hat{c}_\mu^\dagger \qquad \hat{a}_Q = \sum_{\nu} C_{\nu Q} \, \hat{c}_\nu$$

$$\sum_{\mu\nu} \left(\sum_{PQ} C_{\mu P} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, C_{\nu Q} \right) \hat{c}_\mu^\dagger \hat{c}_\nu$$

$$\overline{h}_{\mu\nu}$$

One-electron integrals in the localised orbital basis

Hamiltonian in the localised representation

Delocalized *representation*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\Big\| \quad \Big\|$$

$$\sum_{\mu\nu} \overline{h}_{\mu\nu} \, \hat{c}_\mu^\dagger \hat{c}_\nu$$

Localized *representation*

Hamiltonian in the localised representation

Delocalized *representation*

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\Vert \qquad\qquad \Vert$$

$$\sum_{\mu\nu} \bar{h}_{\mu\nu} \, \hat{c}_\mu^\dagger \hat{c}_\nu \qquad\qquad \frac{1}{2} \sum_{\mu\nu\lambda\tau} \bar{g}_{\mu\nu\tau\lambda} \, \hat{c}_\mu^\dagger \hat{c}_\nu^\dagger \hat{c}_\lambda \hat{c}_\tau$$

Localized *representation* ***Localized*** *representation*

Hamiltonian in the localised representation

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

$$\Big\Vert$$

$$\frac{1}{2} \sum_{\mu\nu\lambda\tau} \overline{g}_{\mu\nu\tau\lambda} \, \hat{c}_\mu^\dagger \hat{c}_\nu^\dagger \hat{c}_\lambda \hat{c}_\tau$$

Two-electron integrals in the localised orbital basis

$$\sum_{PQRS} C_{\mu P} C_{\nu Q} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, C_{\tau R} C_{\lambda S}$$

In summary…

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Delocalized *representation*

|||

Localized *representation*

$$\sum_{\mu\nu} \overline{h}_{\mu\nu} \, \hat{c}_\mu^\dagger \hat{c}_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\tau} \overline{g}_{\mu\nu\tau\lambda} \, \hat{c}_\mu^\dagger \hat{c}_\nu^\dagger \hat{c}_\lambda \hat{c}_\tau$$

In summary…

$$\hat{H} \equiv \sum_{\mu,\nu=1}^{\mathscr{M}} \overline{h}_{\mu\nu}\, \hat{c}_{\mu}^{\dagger}\hat{c}_{\nu} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\tau=1}^{\mathscr{M}} \overline{g}_{\mu\nu\tau\lambda}\, \hat{c}_{\mu}^{\dagger}\hat{c}_{\nu}^{\dagger}\hat{c}_{\lambda}\hat{c}_{\tau}$$

In summary…

$$\hat{H} \equiv \sum_{P,Q=1}^{\mathscr{M}} \overline{h}_{PQ}\, \hat{c}_P^{\dagger} \hat{c}_Q + \frac{1}{2} \sum_{P,Q,R,S=1}^{\mathscr{M}} \overline{g}_{PQRS}\, \hat{c}_P^{\dagger} \hat{c}_Q^{\dagger} \hat{c}_S \hat{c}_R$$

just labels…

In summary…

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Delocalized *representation*

$$\Big\Vert$$

$$\sum_{PQ} \overline{h}_{PQ} \hat{c}_P^\dagger \hat{c}_Q + \frac{1}{2} \sum_{PQRS} \overline{g}_{PQRS} \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R$$

Localized *representation*

Reduced density matrices

$$E_0 = \langle \hat{H} \rangle_{\Psi_0}$$

Reduced density matrices

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Reduced density matrices

$$E_0 = \langle \hat{H} \rangle_{\Psi_0}$$

$$= \sum_{PQ} \overline{h}_{PQ} \langle \hat{c}^\dagger_P \hat{c}_Q \rangle_{\Psi_0} + \frac{1}{2} \sum_{PQRS} \overline{g}_{PQRS} \langle \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

Reduced density matrices

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One-electron reduced density matrix (1RDM)

$$\gamma_{PQ} = \langle \hat{c}^\dagger_P \hat{c}_Q \rangle_{\Psi_0}$$

Reduced density matrices

$$E_0 = \langle \hat{H} \rangle_{\Psi_0}$$

$$= \sum_{PQ} \bar{h}_{PQ} \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0} + \frac{1}{2} \sum_{PQRS} \bar{g}_{PQRS} \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

One-electron reduced density matrix (1RDM)

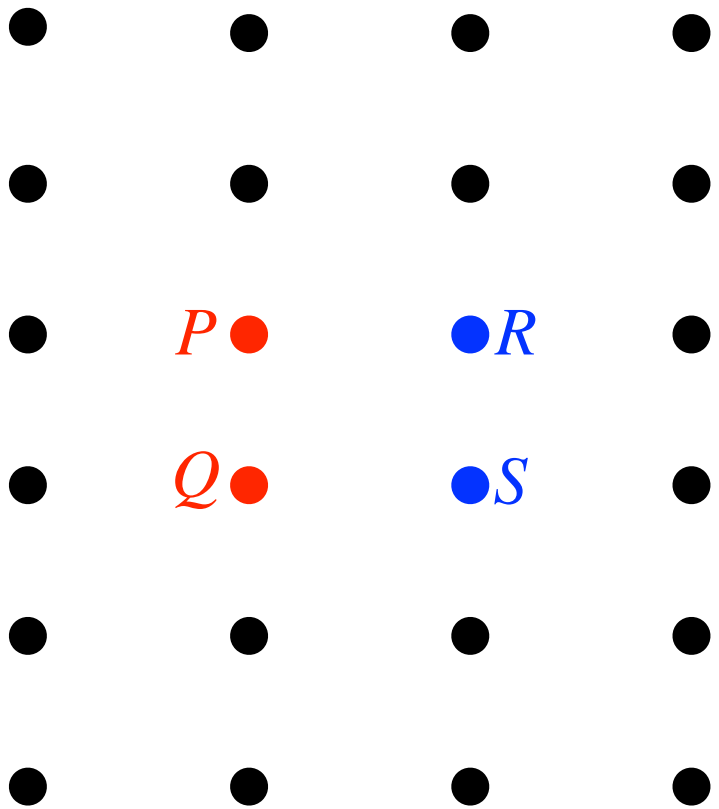
Two-electron reduced density matrix (2RDM)

$$\gamma_{PQ} = \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0}$$

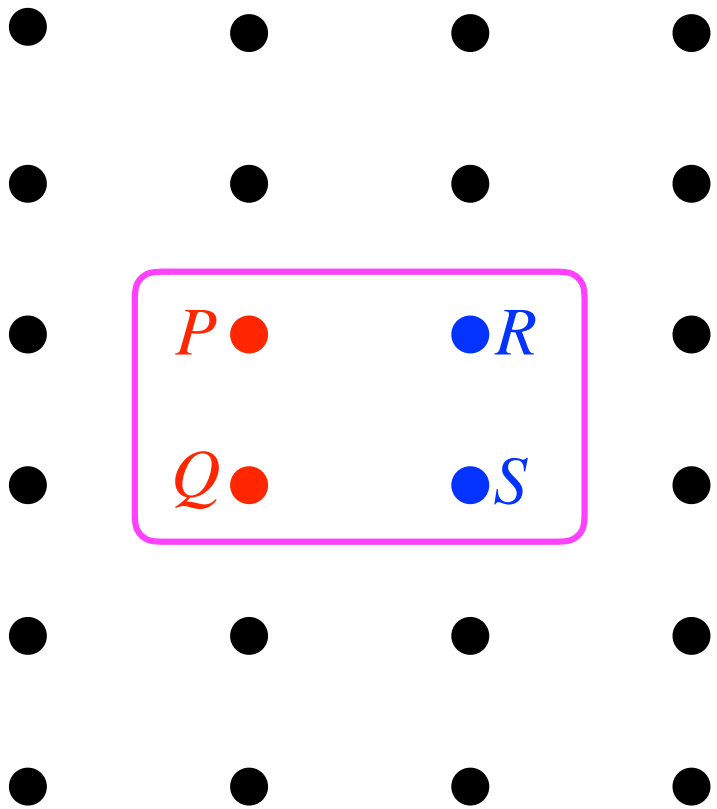
$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

Reduced density matrices

Let's consider a 2D lattice of localised spin-orbitals



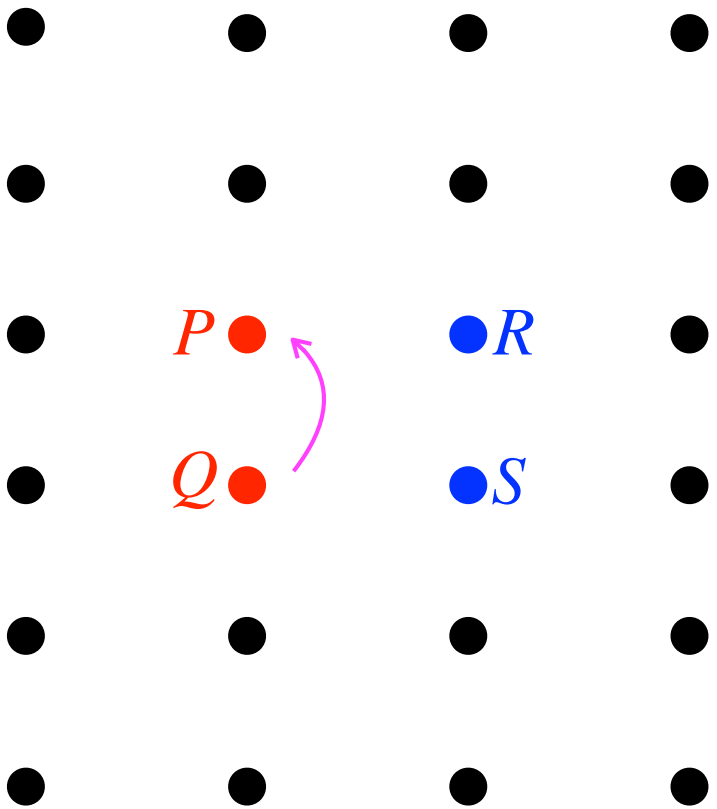
Reduced density matrices



"fragment"

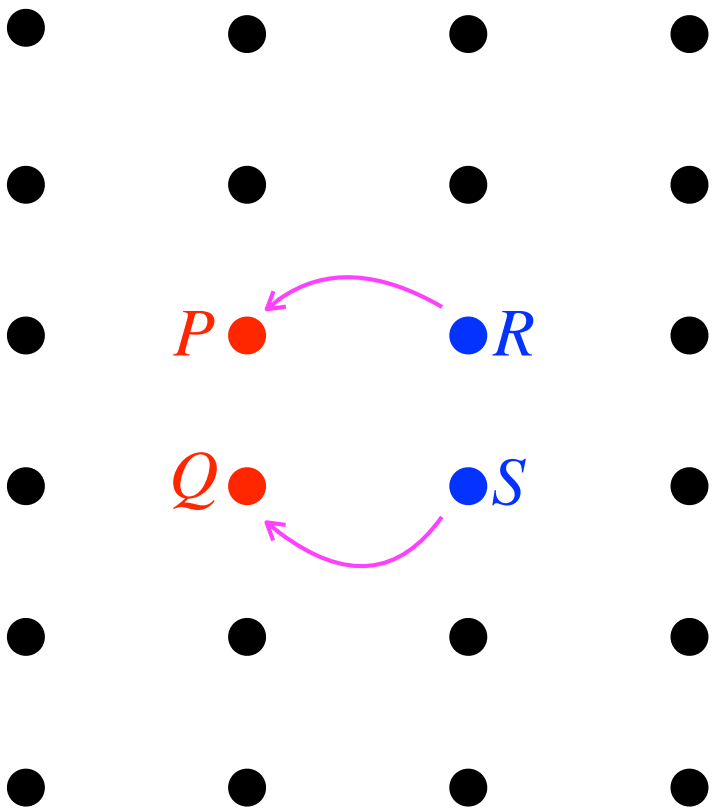
Reduced density matrices

$$\gamma_{PQ} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q | \Psi_0 \rangle$$



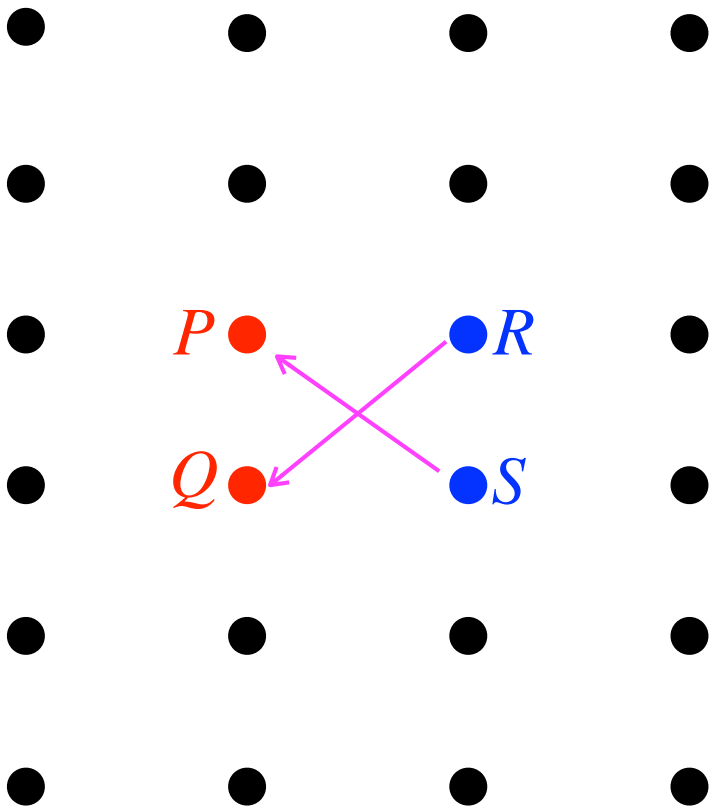
Reduced density matrices

$$\Gamma_{PQSR} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi_0 \rangle$$



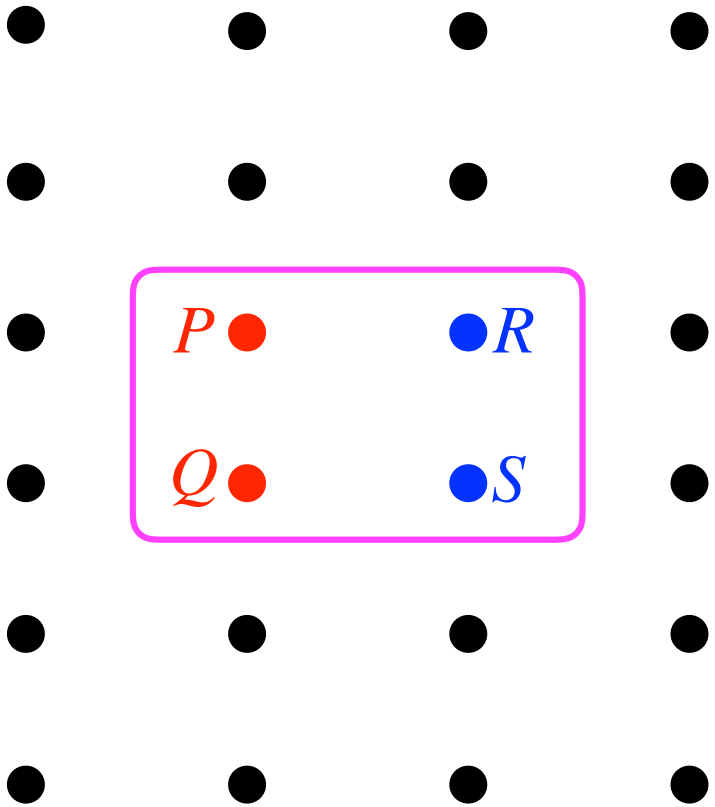
Reduced density matrices

$$\Gamma_{PQSR} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi_0 \rangle$$



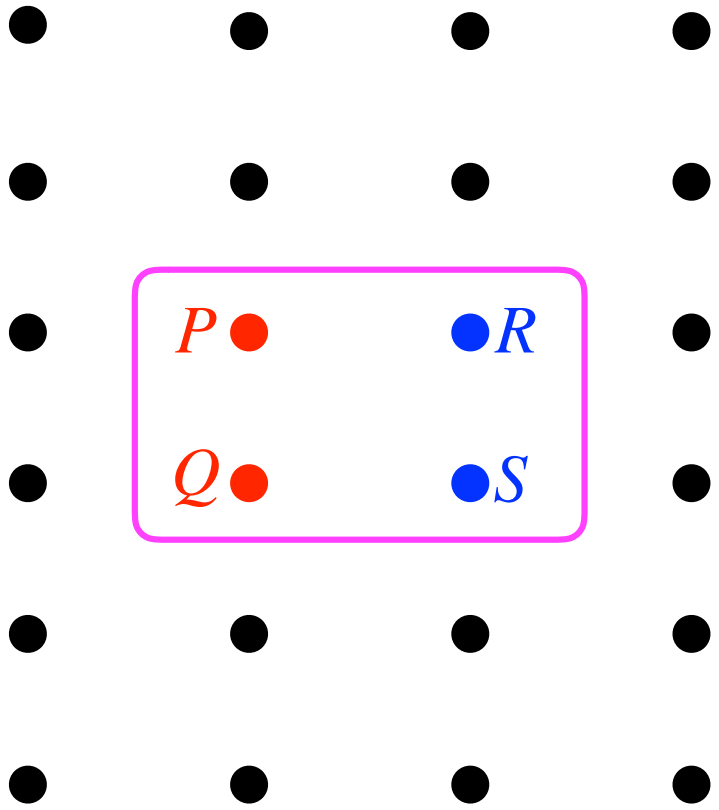
Reduced density matrices

*The $PQRS$ orbital fragment is **NOT disconnected** from the other orbitals*



Reduced density matrices

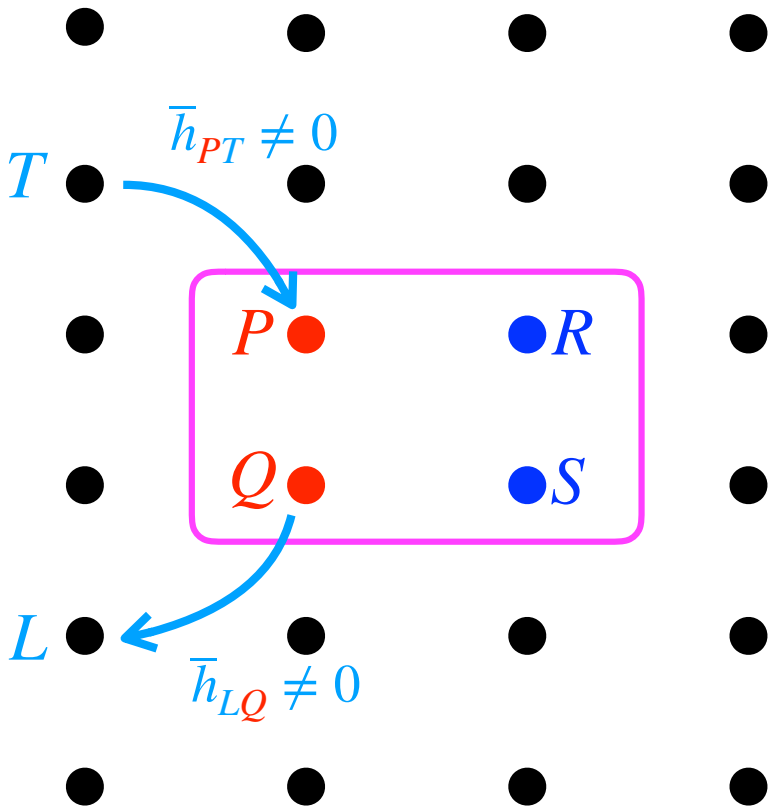
*The $PQRS$ orbital fragment is **NOT disconnected** from the other orbitals*



Open quantum subsystem

Reduced density matrices

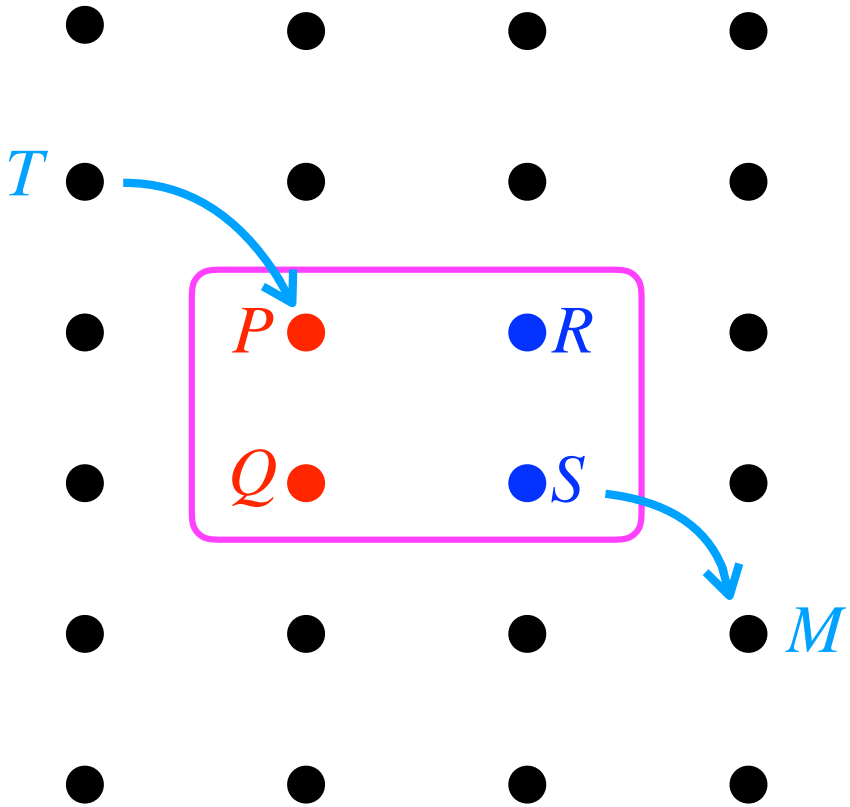
$$\hat{H} \equiv \sum_{PQ} \bar{h}_{PQ}\, \hat{c}_P^\dagger \hat{c}_Q + \frac{1}{2} \sum_{PQRS} \bar{g}_{PQRS}\, \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R$$



Entanglement

Reduced density matrices

$$\hat{H} \equiv \sum_{PQ} \bar{h}_{PQ}\, \hat{c}_P^\dagger \hat{c}_Q + \frac{1}{2} \sum_{PQRS} \bar{g}_{PQRS}\, \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R$$



$$\bar{g}_{PMTS} \neq 0$$

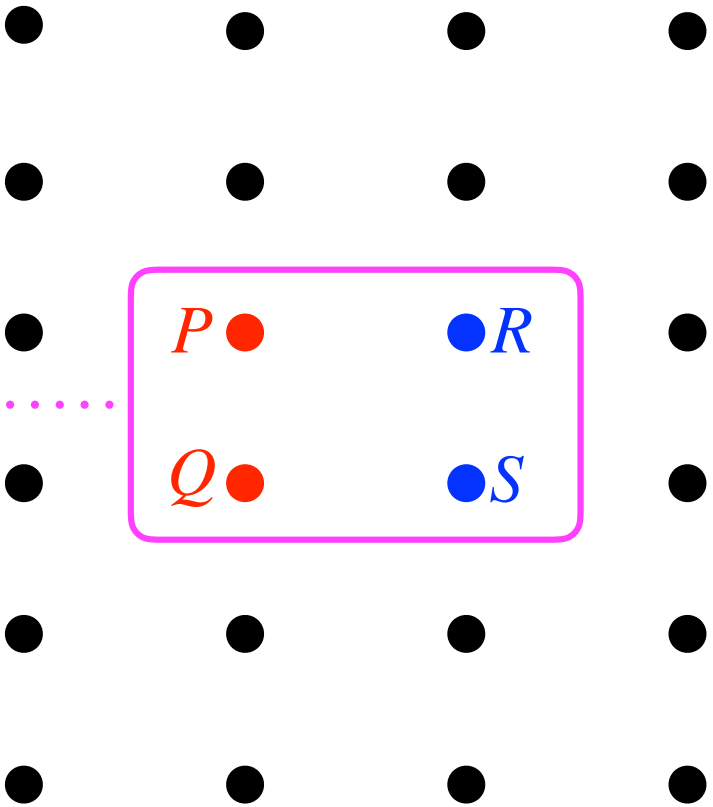
Entanglement

Reduced density matrices

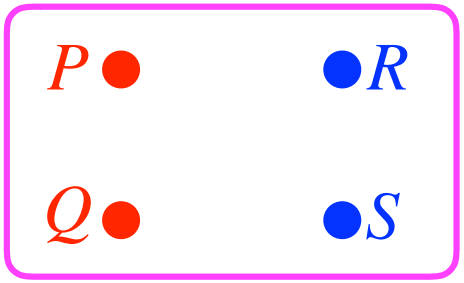
The evaluation of the RDMs requires, in principle, the ***full wave function*** Ψ_0

$$\gamma_{PQ} = \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0}$$

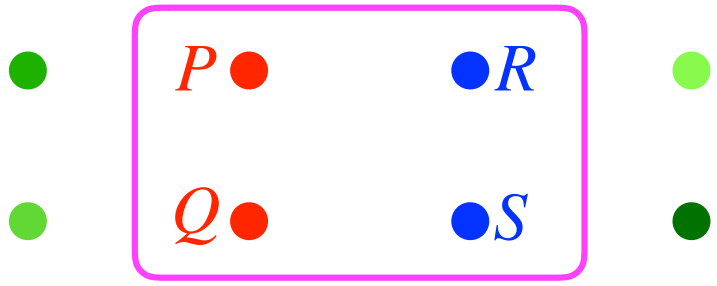
$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$



Embedding of localised spin-orbitals



Embedding of localised spin-orbitals

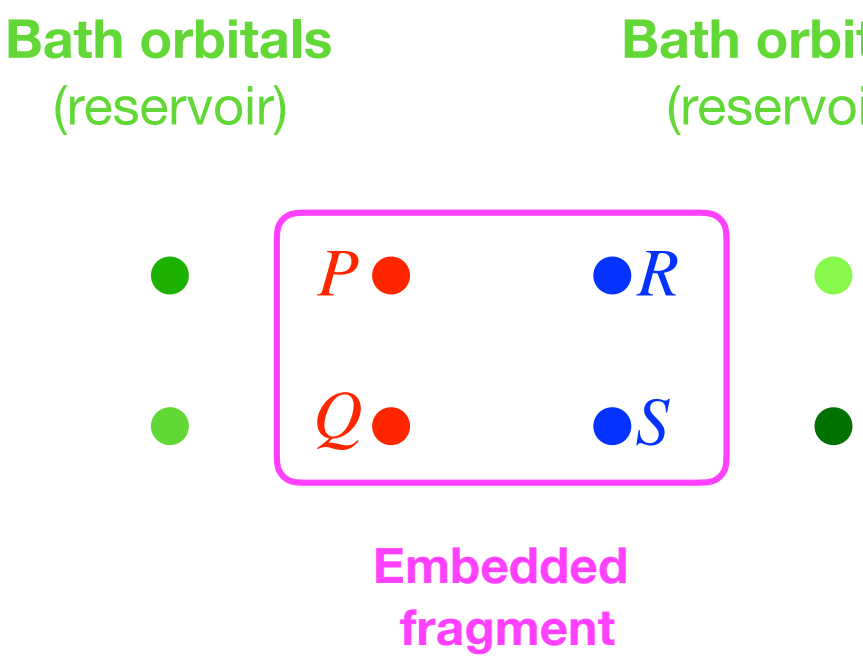


Embedding of localised spin-orbitals

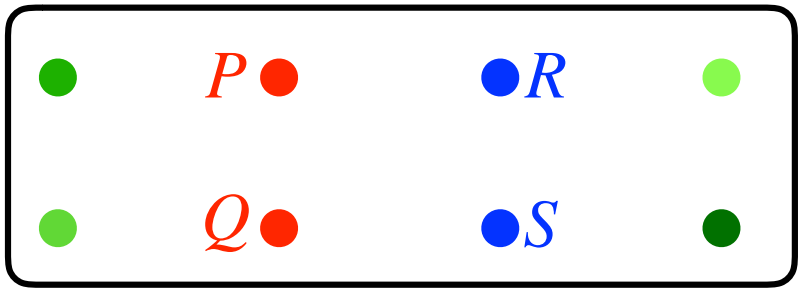
Bath orbitals
(reservoir)

Bath orbitals
(reservoir)

Embedding of localised spin-orbitals



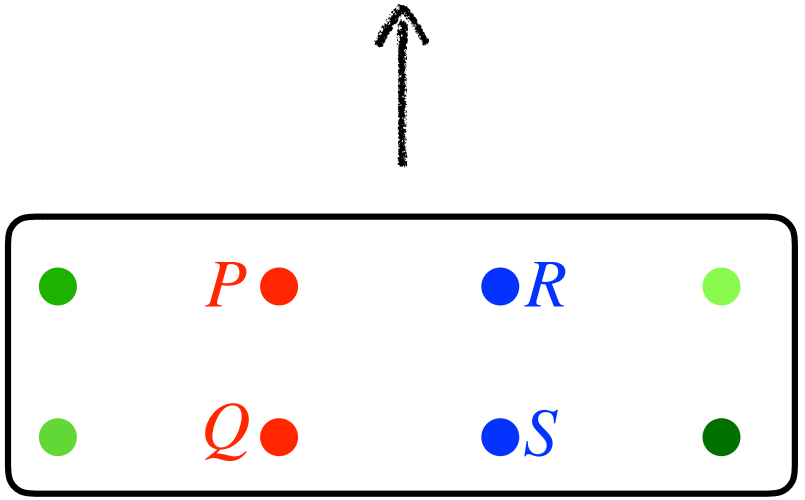
Embedding of localised spin-orbitals



Cluster

Embedding of localised spin-orbitals

Closed *(and much smaller than the true system)*



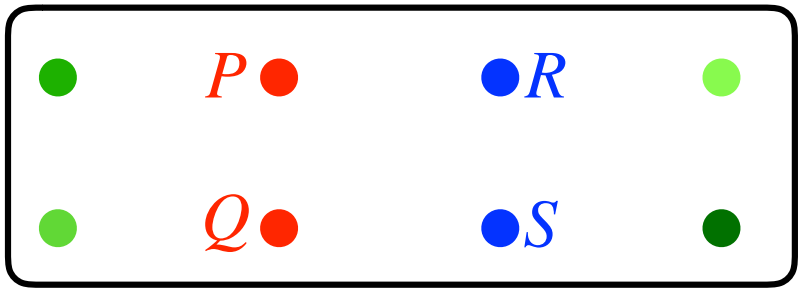
$\Psi^{\mathscr{C}}$

Cluster

Embedding of localised spin-orbitals

$$\gamma_{PQ} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q | \Psi_0 \rangle \approx \langle \Psi^{\mathscr{C}} | \hat{c}_P^\dagger \hat{c}_Q | \Psi^{\mathscr{C}} \rangle$$

$$\Gamma_{PQSR} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi_0 \rangle \approx \langle \Psi^{\mathscr{C}} | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi^{\mathscr{C}} \rangle$$



$\Psi^{\mathscr{C}}$

Cluster

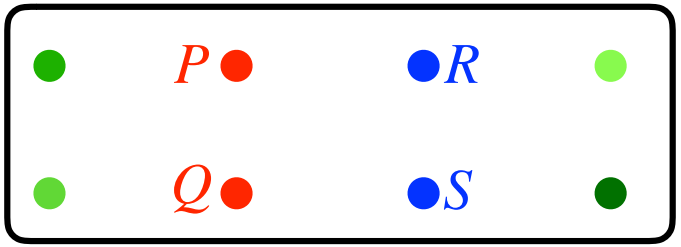
Embedding of localised spin-orbitals

$$\gamma_{PQ} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q | \Psi_0 \rangle \approx \langle \Psi^{\mathscr{C}} | \hat{c}_P^\dagger \hat{c}_Q | \Psi^{\mathscr{C}} \rangle$$

$$\Gamma_{PQSR} = \langle \Psi_0 | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi_0 \rangle \approx \langle \Psi^{\mathscr{C}} | \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R | \Psi^{\mathscr{C}} \rangle$$

Key idea of

density matrix embedding theory (DMET)*



$\Psi^{\mathscr{C}}$

Cluster

*G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109***, 186404 (2012).