Quantum embedding in electronic structure theory

Part 2: Concept of embedding and its various formulations

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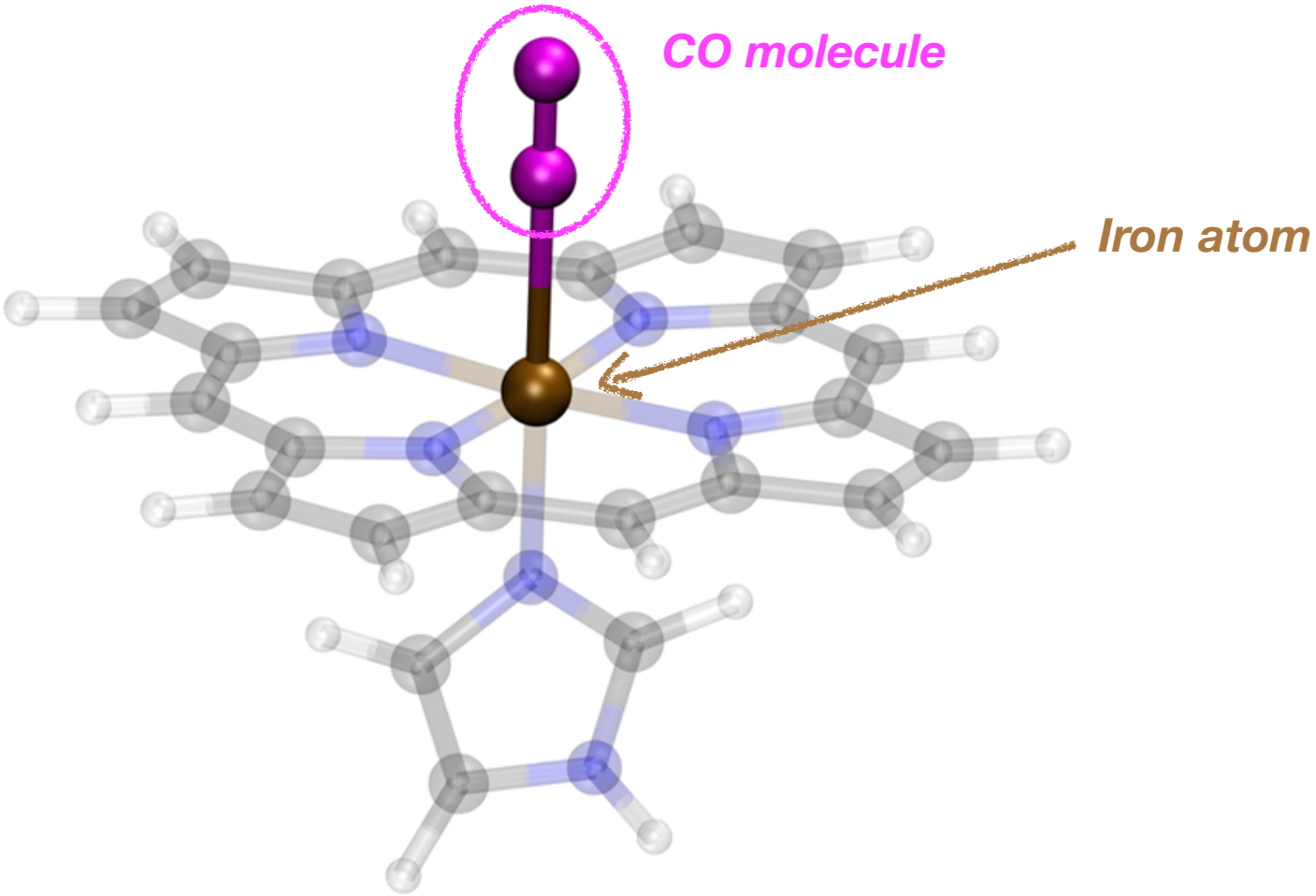
CO Binding in an Iron–Porphyrin Complex



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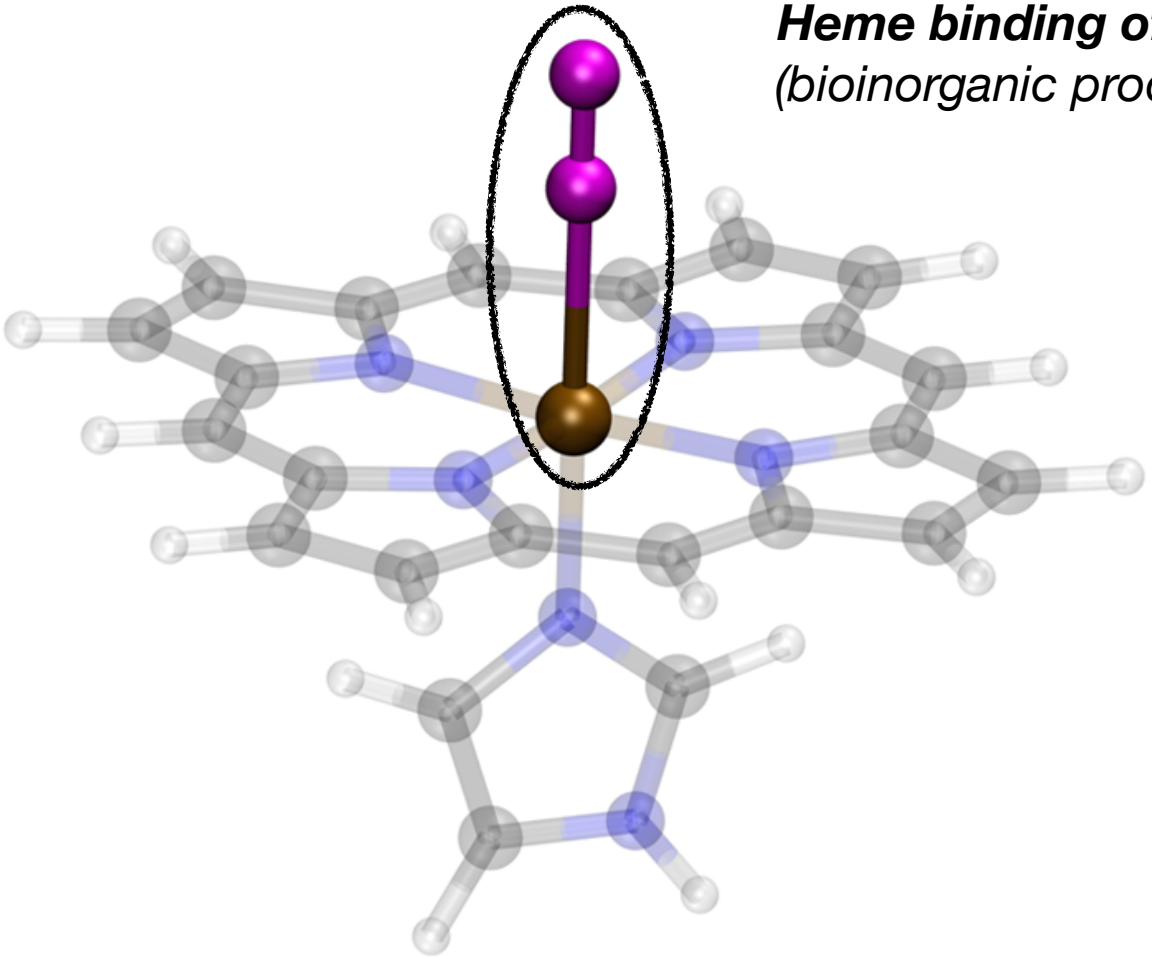
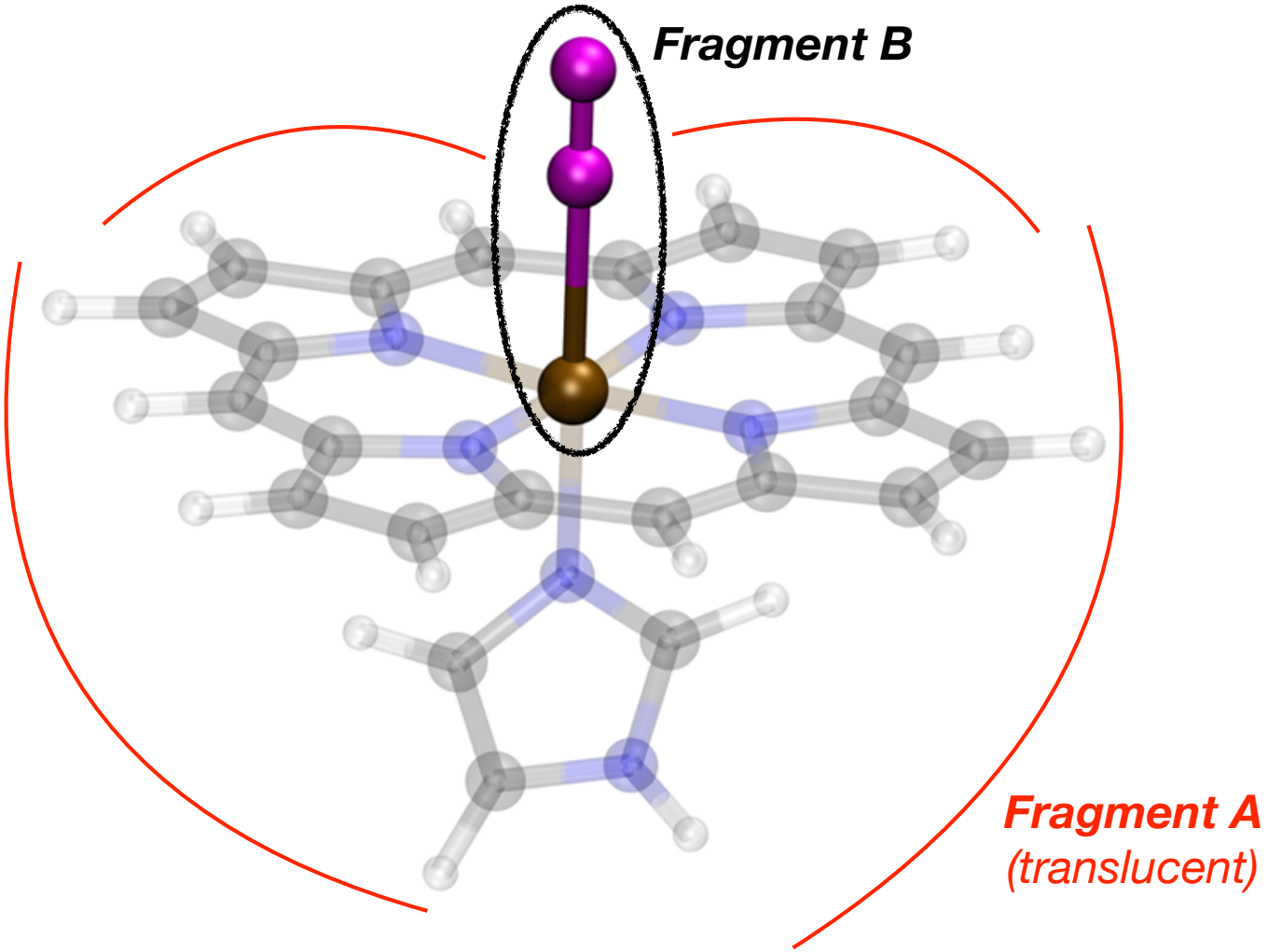


Heme binding of CO
(bioinorganic process)

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

CO Binding in an Iron–Porphyrin Complex



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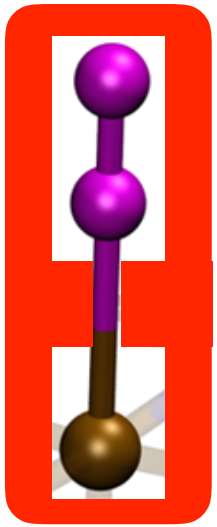
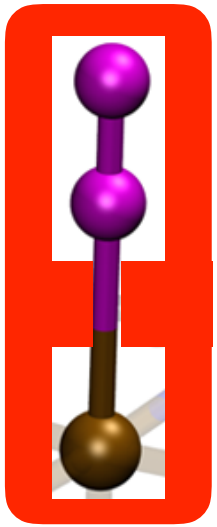


To-be-described embedded fragment B

CO Binding in an Iron–Porphyrin Complex



To-be-described embedded fragment B

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

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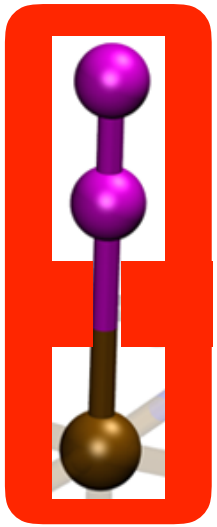
CO Binding in an Iron–Porphyrin Complex



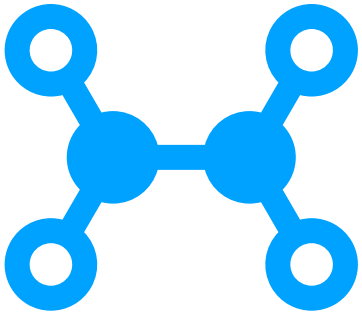
To-be-described embedded fragment B

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

?

Strategy 1: DFT-based quantum embedding approach

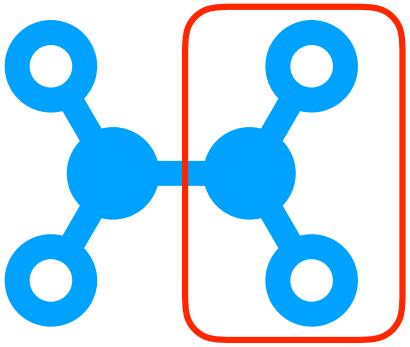
Frozen density embedding theory



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

Frozen density embedding theory

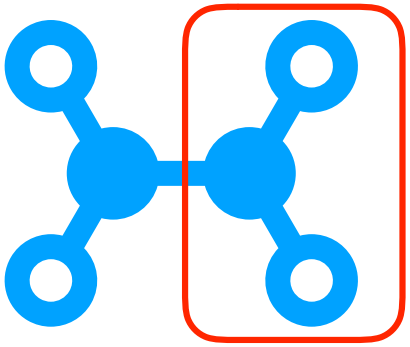
Fragment A



$n_A(\mathbf{r})$ ⟵ *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

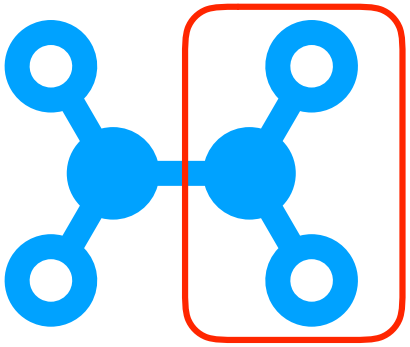
Total number of electrons in the molecule

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

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

Frozen density embedding theory

Fragment A



$n_A(\mathbf{r})$

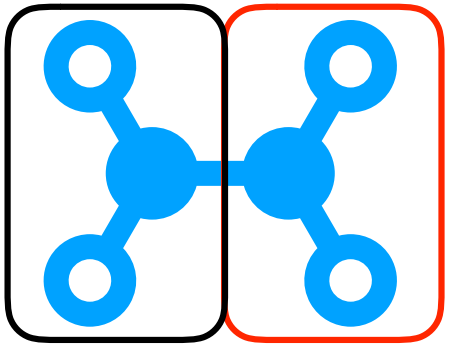
Density *giving an approximate description of a molecular* *fragment*

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 B **Fragment A**

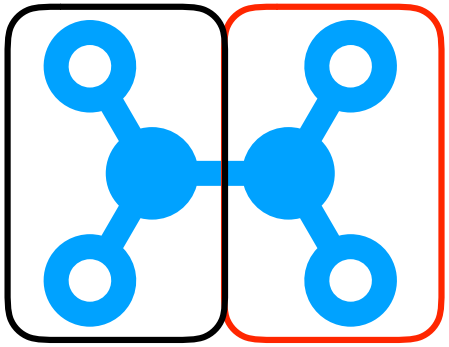


$n_A(\mathbf{r})$ ***known***

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

Frozen density embedding theory

Fragment B **Fragment A**

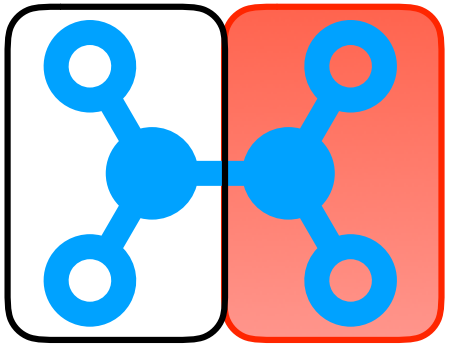


$n_A(\mathbf{r})$ ***known***

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

Frozen density embedding theory

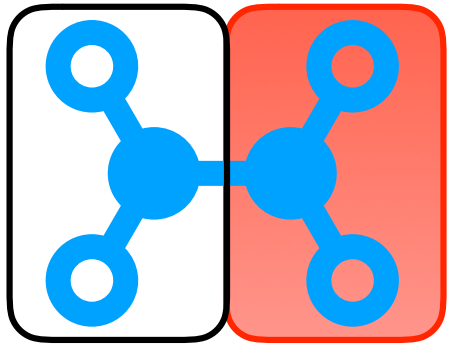
Fragment B



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

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

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

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

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

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*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

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

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

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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

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

Variational principle for fragment B

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

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

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

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Described with KS orbitals
in KS-DFT

Variational principle for fragment B

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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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More difficult
to approximate with density functionals

Variational principle for fragment B

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

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 need to write the Hamiltonian in **second quantization** for that purpose*

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

Second-quantized encoding of many-electron wave functions

Hydrogen molecule in the dissociation limit:

$$\sqrt{2}\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)$$

Second-quantized encoding of many-electron wave functions

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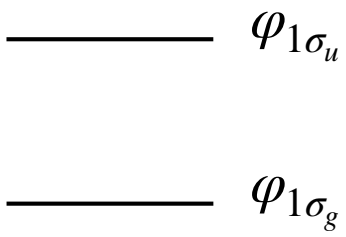
$$\sqrt{2}\,|\Psi_0\rangle = \left|\begin{array}{l}\varphi_{1\sigma_u}\\ \varphi_{1\sigma_g}\end{array}\right\rangle - \left|\begin{array}{l}\varphi_{1\sigma_u}\\ \varphi_{1\sigma_g}\end{array}\right\rangle$$

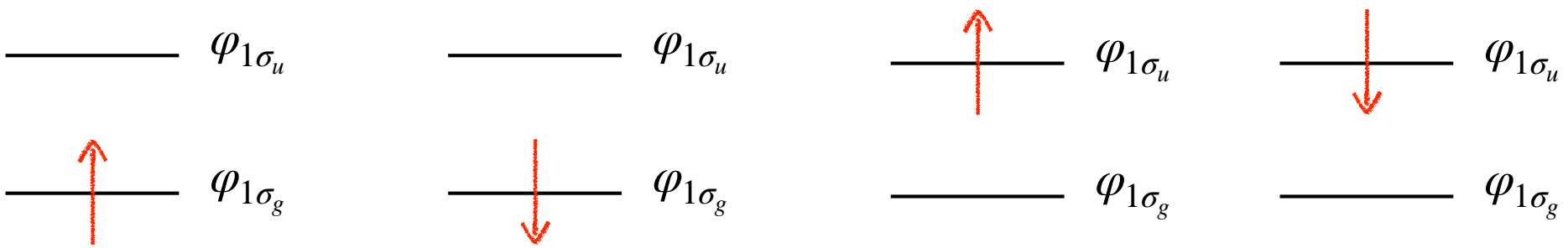
Dirac notation

Second-quantized encoding of many-electron wave functions



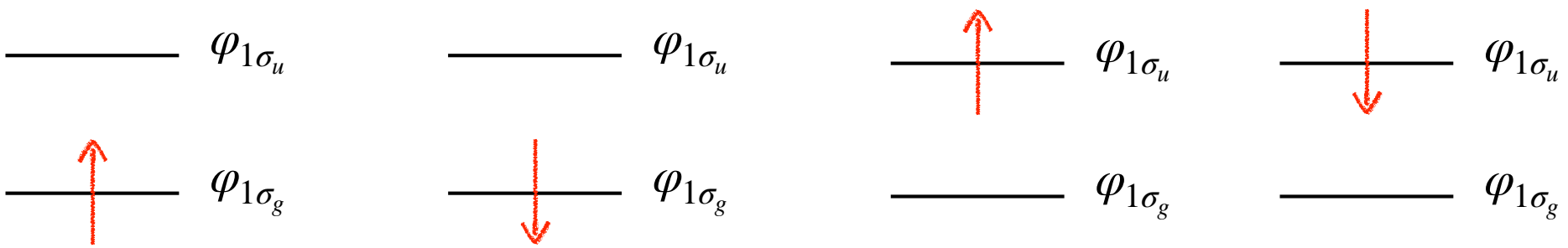
Zero-electron *(vacuum) quantum state*

One-electron *quantum states*



$|\varphi_1\rangle$ $|\varphi_2\rangle$ $|\varphi_3\rangle$ $|\varphi_4\rangle$

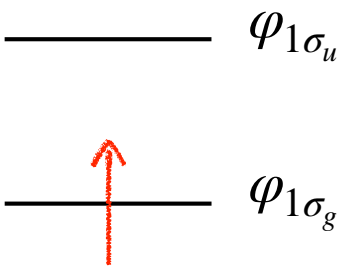
One-electron *quantum states*



$|\varphi_1\rangle$ $|\varphi_2\rangle$ $|\varphi_3\rangle$ $|\varphi_4\rangle$

Spin-orbitals

One-electron *quantum states*



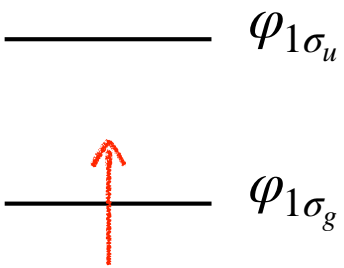
$\equiv$

Second quantization
notation

$$\hat{a}_1^\dagger \left| \begin{array}{l} \varphi_{1\sigma_u} \\ \varphi_{1\sigma_g} \end{array} \right\rangle$$

$$|\varphi_1\rangle$$

One-electron *quantum states*



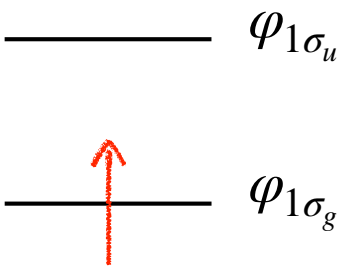
$|\varphi_1\rangle$

$\equiv$

$\hat{a}_1^\dagger \left| \begin{array}{l} \varphi_{1\sigma_u} \\ \varphi_{1\sigma_g} \end{array} \right\rangle$

Quantum operator that ***creates*** *an electron and put it in the spin-orbital* φ_1

One-electron *quantum states*



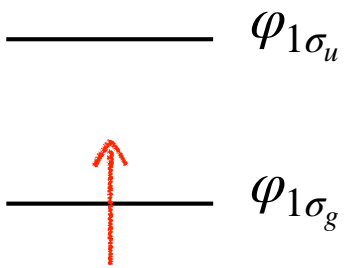
$\equiv$

$$\hat{a}_1^\dagger \left| \begin{array}{l} \varphi_{1\sigma_u} \\ \varphi_{1\sigma_g} \end{array} \right\rangle$$

Creation operator

$|\varphi_1\rangle$

One-electron *quantum states*



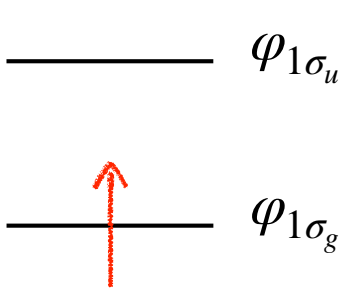
$$|\varphi_1\rangle$$

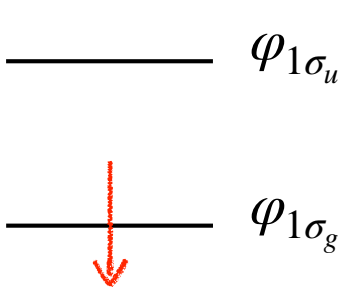
$$\hat{a}_1^\dagger \left| \begin{array}{l} \text{——} \; \varphi_{1\sigma_u} \\ \text{——} \; \varphi_{1\sigma_g} \end{array} \right\rangle$$

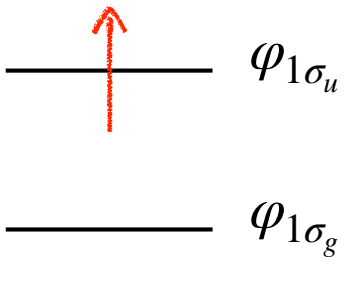
$$|\varphi_1\rangle \equiv \hat{a}_1^\dagger |\text{vac}\rangle$$

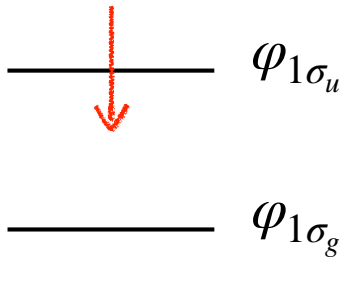
Second-quantized notation

One-electron *quantum states*



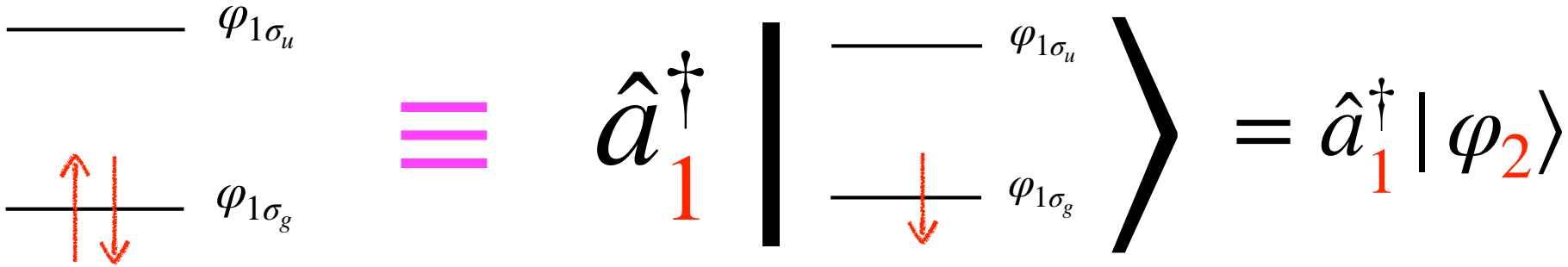




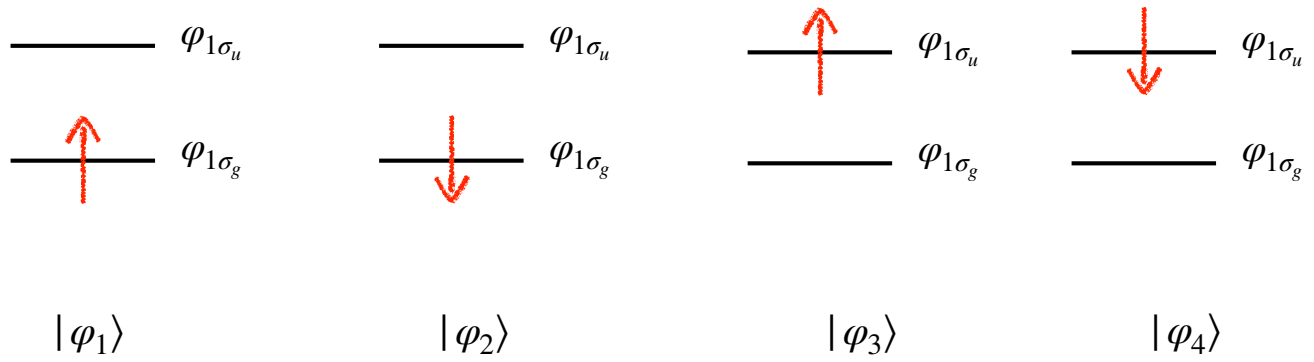


$$|\varphi_1\rangle \equiv \hat{a}_1^\dagger |\text{vac}\rangle \qquad |\varphi_2\rangle \equiv \hat{a}_2^\dagger |\text{vac}\rangle \qquad |\varphi_3\rangle \equiv \hat{a}_3^\dagger |\text{vac}\rangle \qquad |\varphi_4\rangle \equiv \hat{a}_4^\dagger |\text{vac}\rangle$$

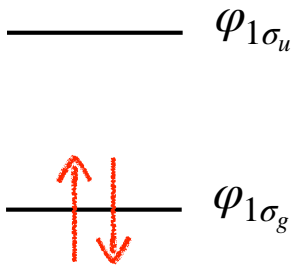
Two-electron *quantum states*



One-electron *quantum states*

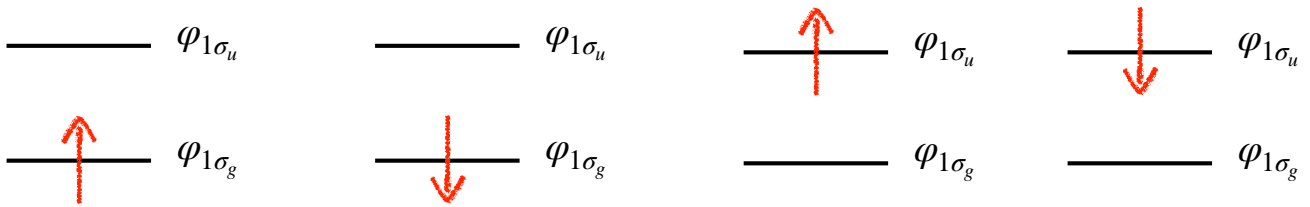


Two-electron *quantum states*



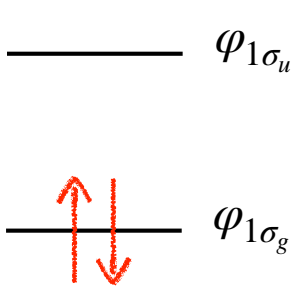
$$\equiv \quad \hat{a}_1^\dagger \hat{a}_2^\dagger \,|\,\mathrm{vac}\rangle$$

One-electron *quantum states*

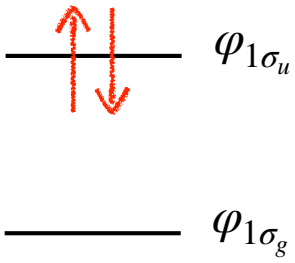


$|\varphi_1\rangle$ $|\varphi_2\rangle$ $|\varphi_3\rangle$ $|\varphi_4\rangle$

Two-electron *quantum states*

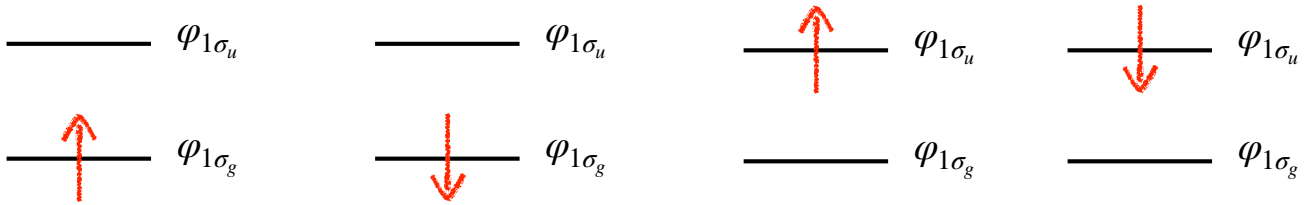


$$\equiv \quad \hat{a}_1^\dagger \hat{a}_2^\dagger \,|\,\mathrm{vac}\rangle$$



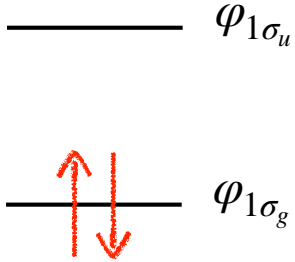
$$\equiv \quad \hat{a}_3^\dagger \hat{a}_4^\dagger \,|\,\mathrm{vac}\rangle$$

One-electron *quantum states*

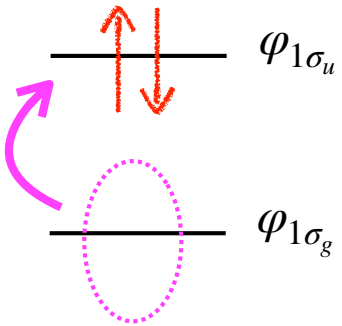


$|\varphi_1\rangle$ $|\varphi_2\rangle$ $|\varphi_3\rangle$ $|\varphi_4\rangle$

Two-electron *quantum states*

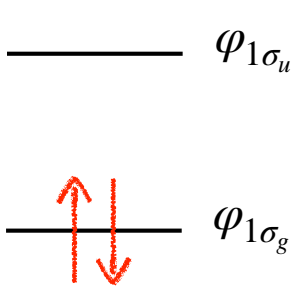


$$\equiv \quad \hat{a}_1^\dagger \hat{a}_2^\dagger \,|\,\mathrm{vac}\rangle$$

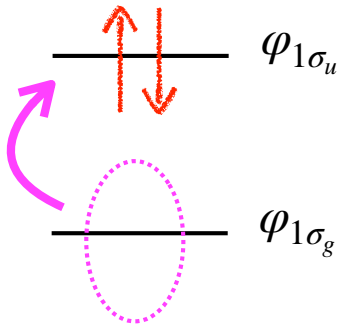


$$\equiv \quad \hat{a}_3^\dagger \hat{a}_4^\dagger \,|\,\mathrm{vac}\rangle$$

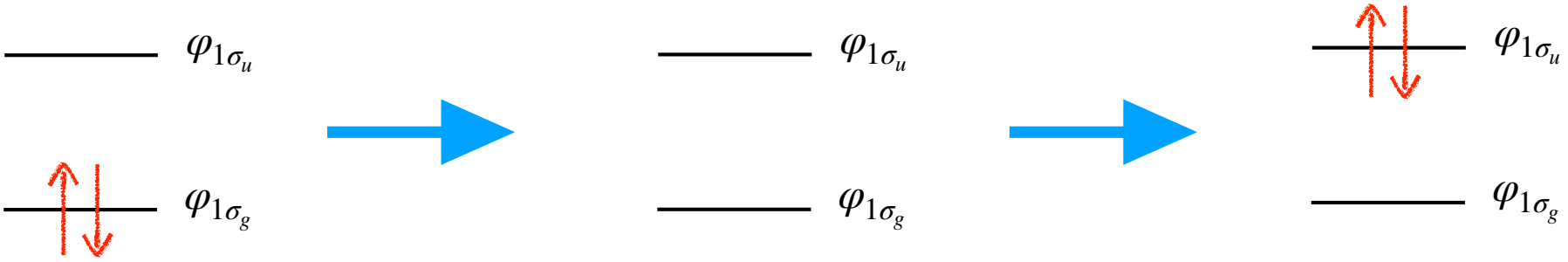
Two-electron *quantum states*



$$\equiv \quad \hat{a}_1^\dagger \hat{a}_2^\dagger \,|\,\mathrm{vac}\rangle$$



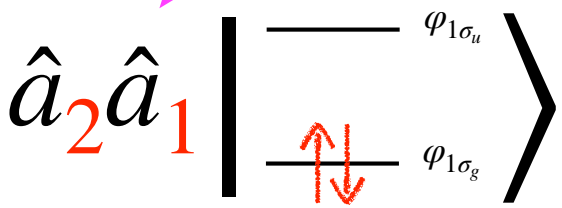
$$\equiv \quad \hat{a}_3^\dagger \hat{a}_4^\dagger \,|\,\mathrm{vac}\rangle$$



$$\equiv$$

$$\hat{a}_2 \hat{a}_1 \left| \right. \left. \right\rangle = |\,\mathrm{vac}\rangle$$

*Quantum operator that **removes***
the electron occupying the spin-orbital φ_1



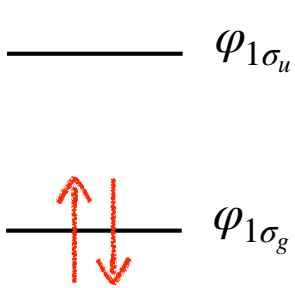
*Quantum operator that **removes***
the electron occupying the spin-orbital φ_2

$$\hat{a}_2\hat{a}_1 \left| \begin{array}{c} \text{———} \; \varphi_{1\sigma_u} \\ \\ \text{——}\uparrow\downarrow\text{——} \; \varphi_{1\sigma_g} \end{array} \right\rangle$$

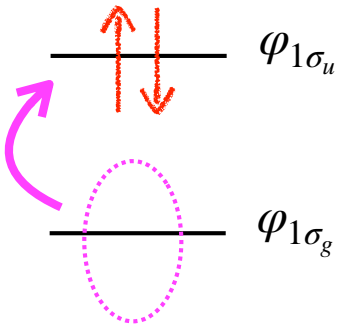
Annihilation operators

$$\hat{a}_2\hat{a}_1 \left| \begin{array}{c} \varphi_{1\sigma_u} \\ \uparrow\downarrow \\ \varphi_{1\sigma_g} \end{array} \right\rangle$$

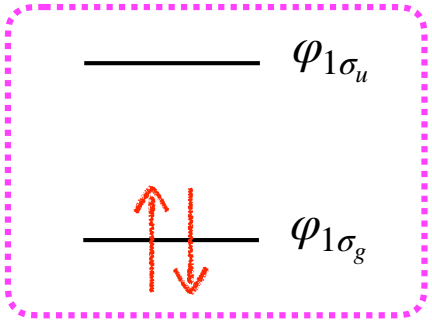
Two-electron *quantum states*

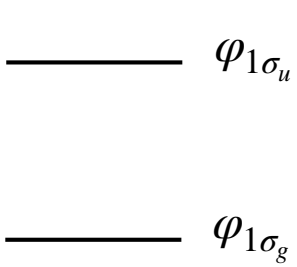


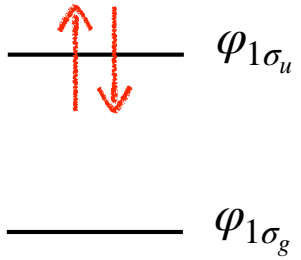
$\equiv \quad \hat{a}_1^\dagger \hat{a}_2^\dagger \,|\,\mathrm{vac}\rangle$



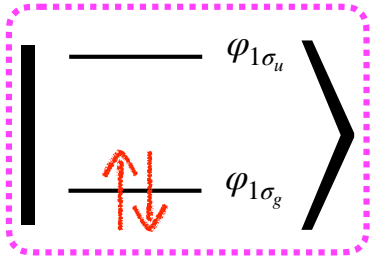
$\equiv \quad \hat{a}_3^\dagger \hat{a}_4^\dagger \,|\,\mathrm{vac}\rangle$







$\equiv\equiv\equiv$

$\hat{a}_3^\dagger \hat{a}_4^\dagger \hat{a}_2 \hat{a}_1 \Big|$  $\Big\rangle$

Double excitation operator

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) 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) 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

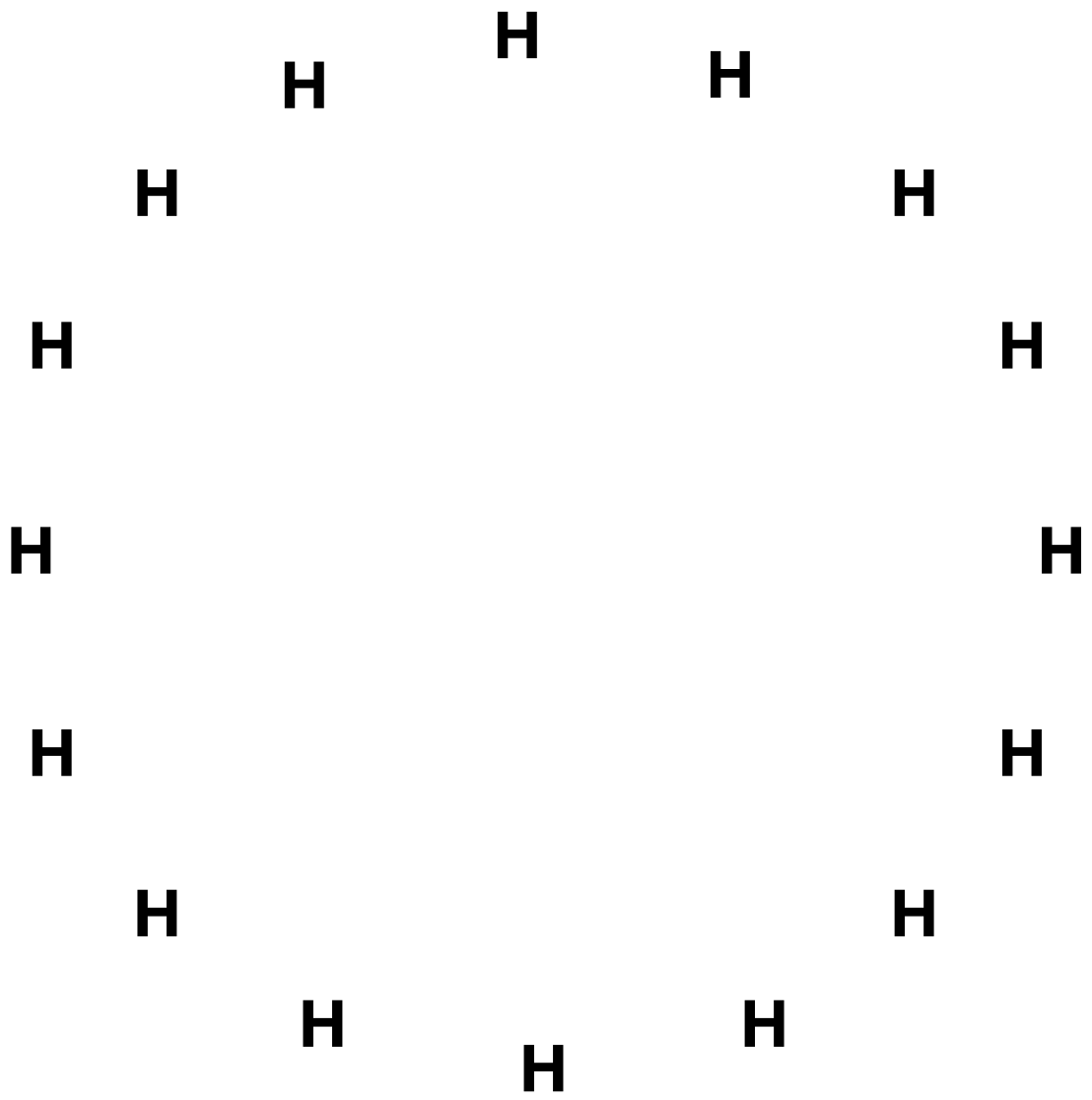
$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

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

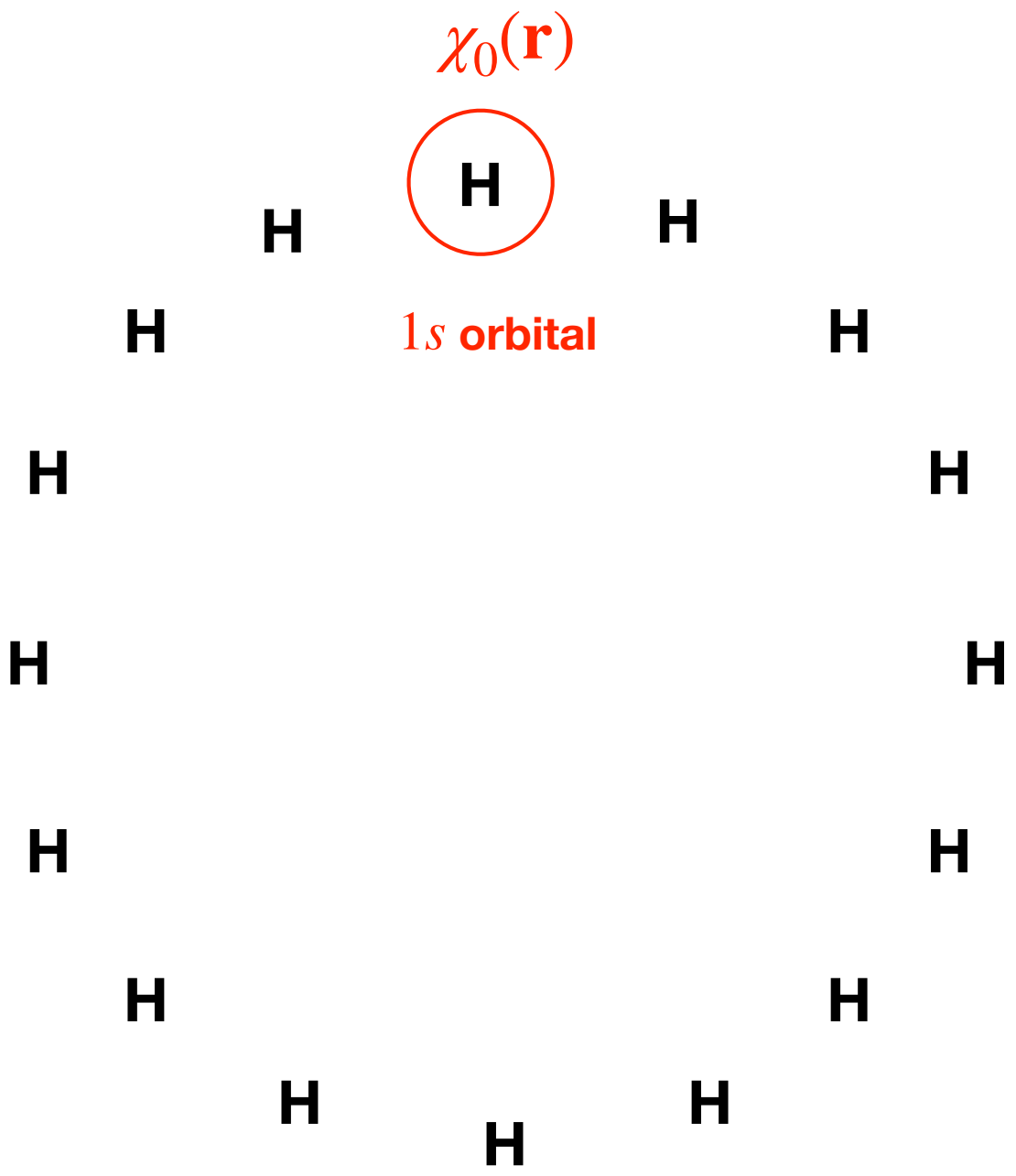
Optimised through energy minimisation

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

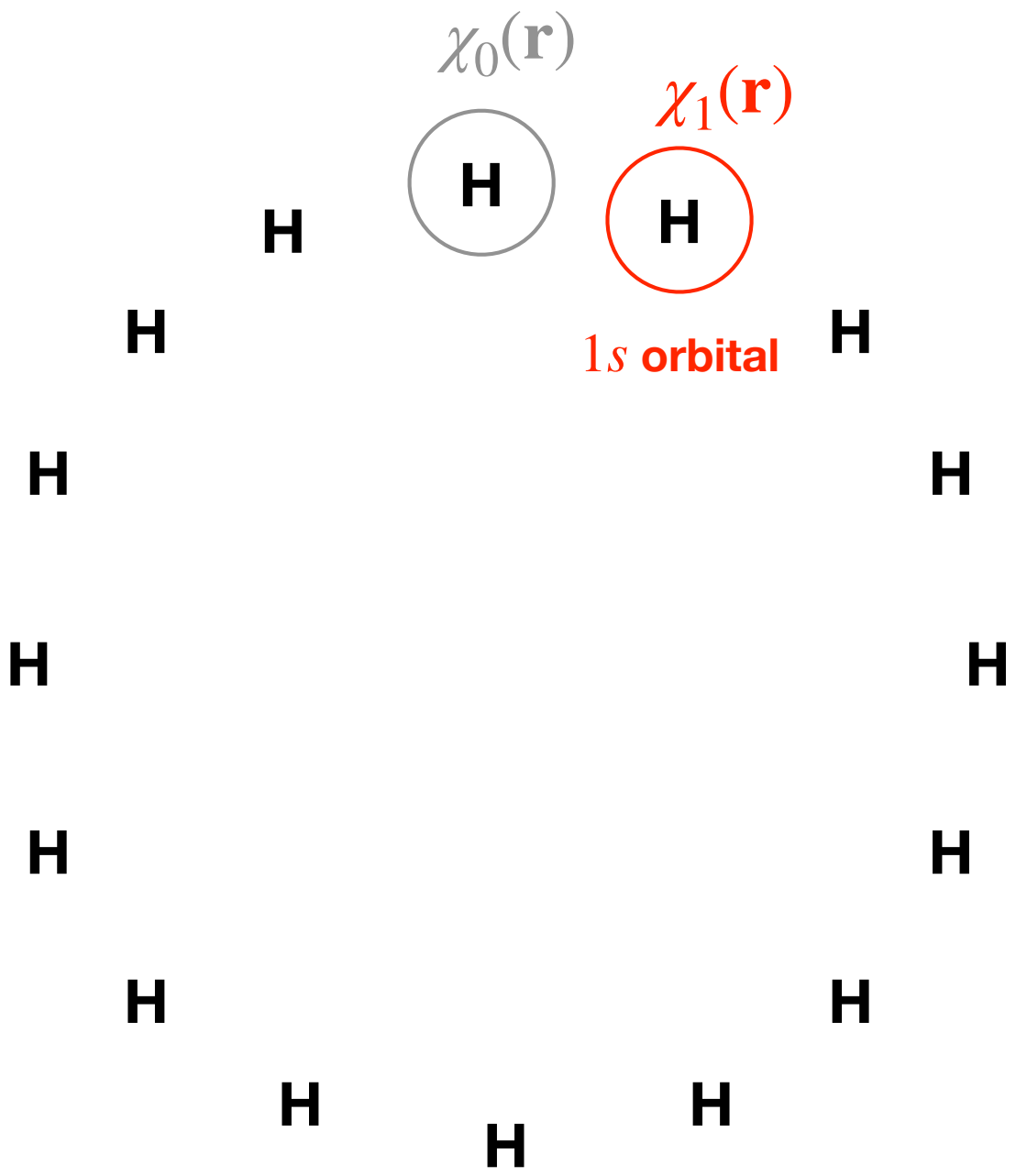
Prototypical ring of $L = 16$ hydrogen atoms



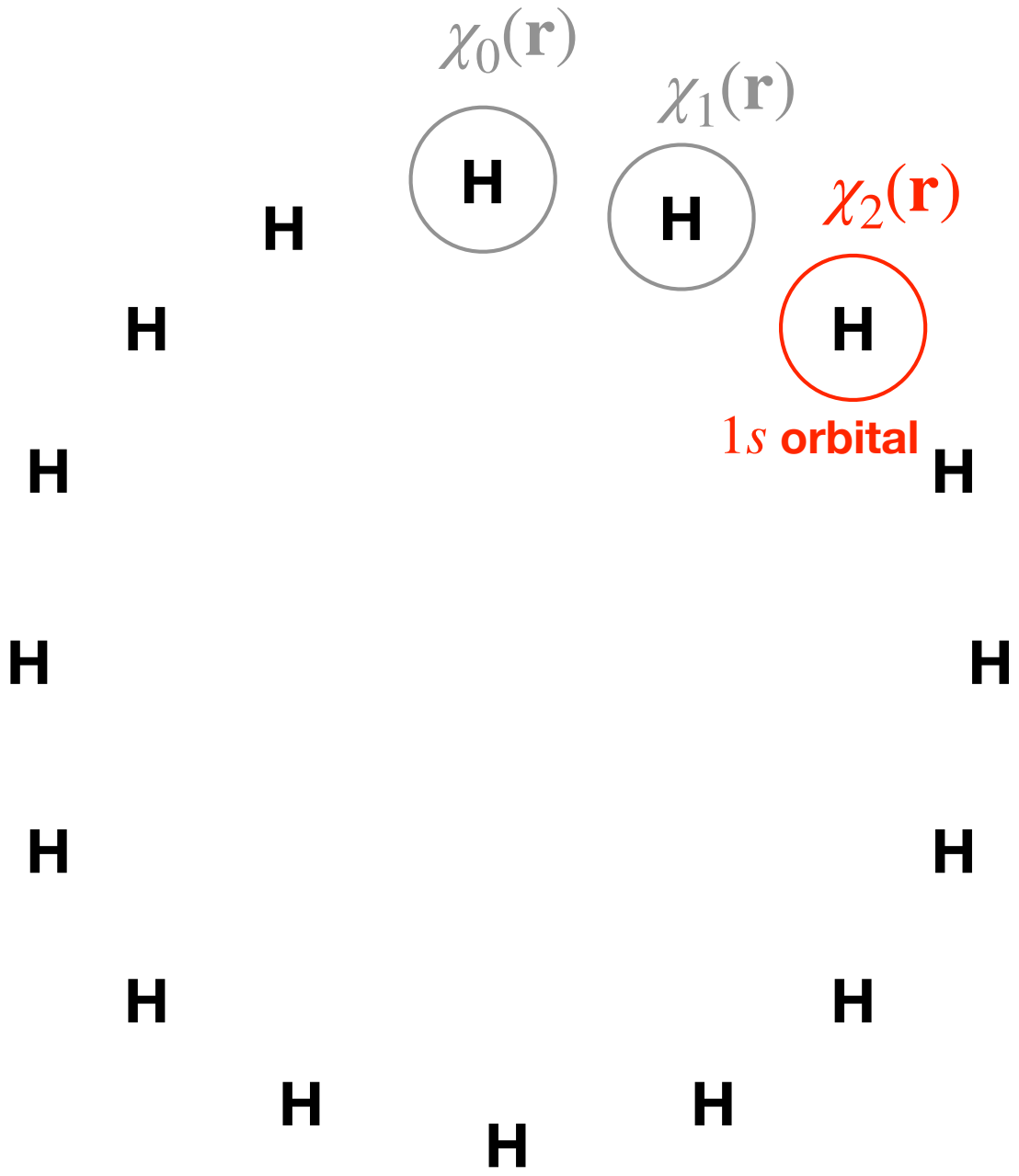
Prototypical ring of $L = 16$ hydrogen atoms



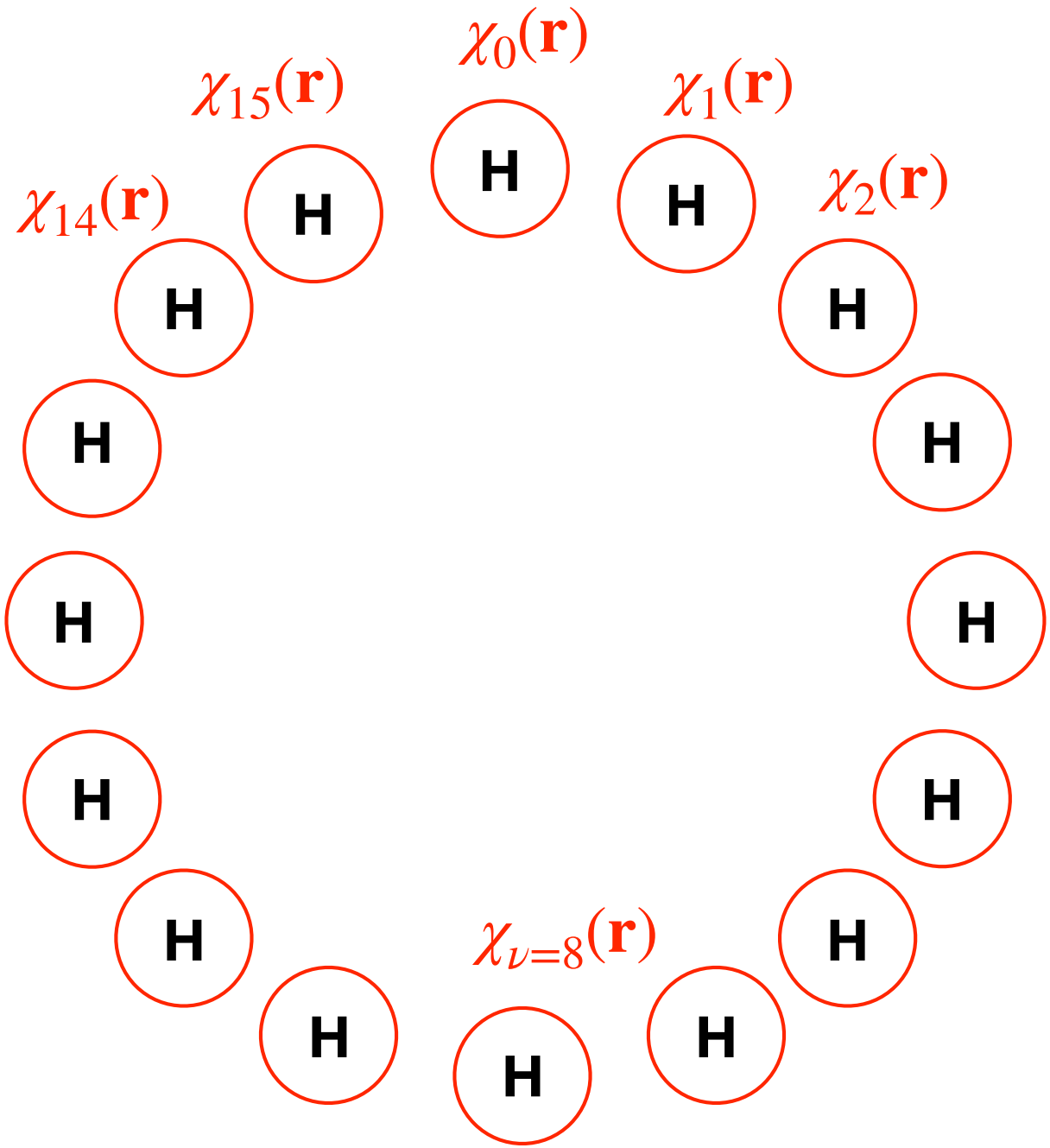
Prototypical ring of $L = 16$ hydrogen atoms



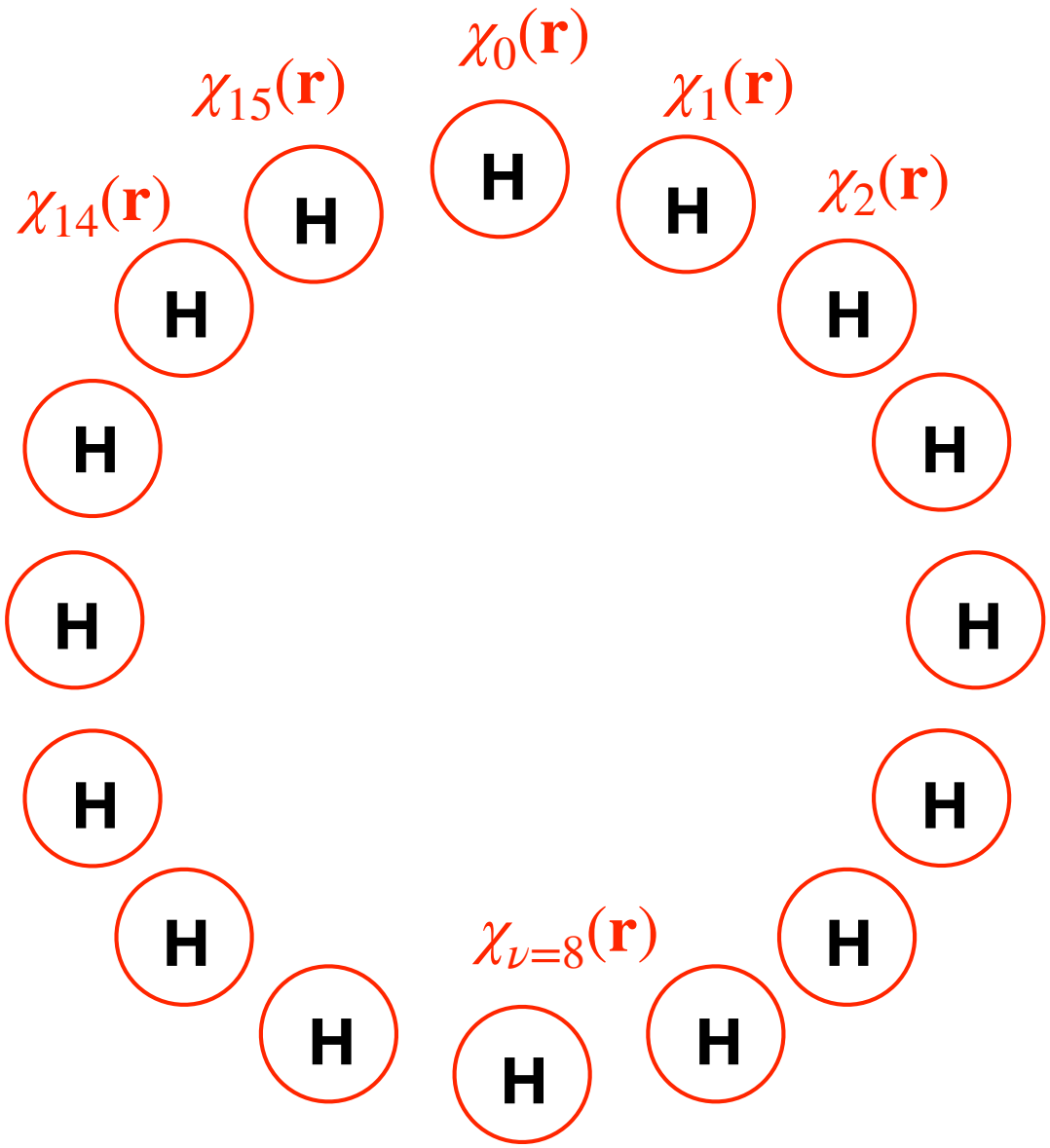
Prototypical ring of $L = 16$ hydrogen atoms



Prototypical ring of $L = 16$ hydrogen atoms



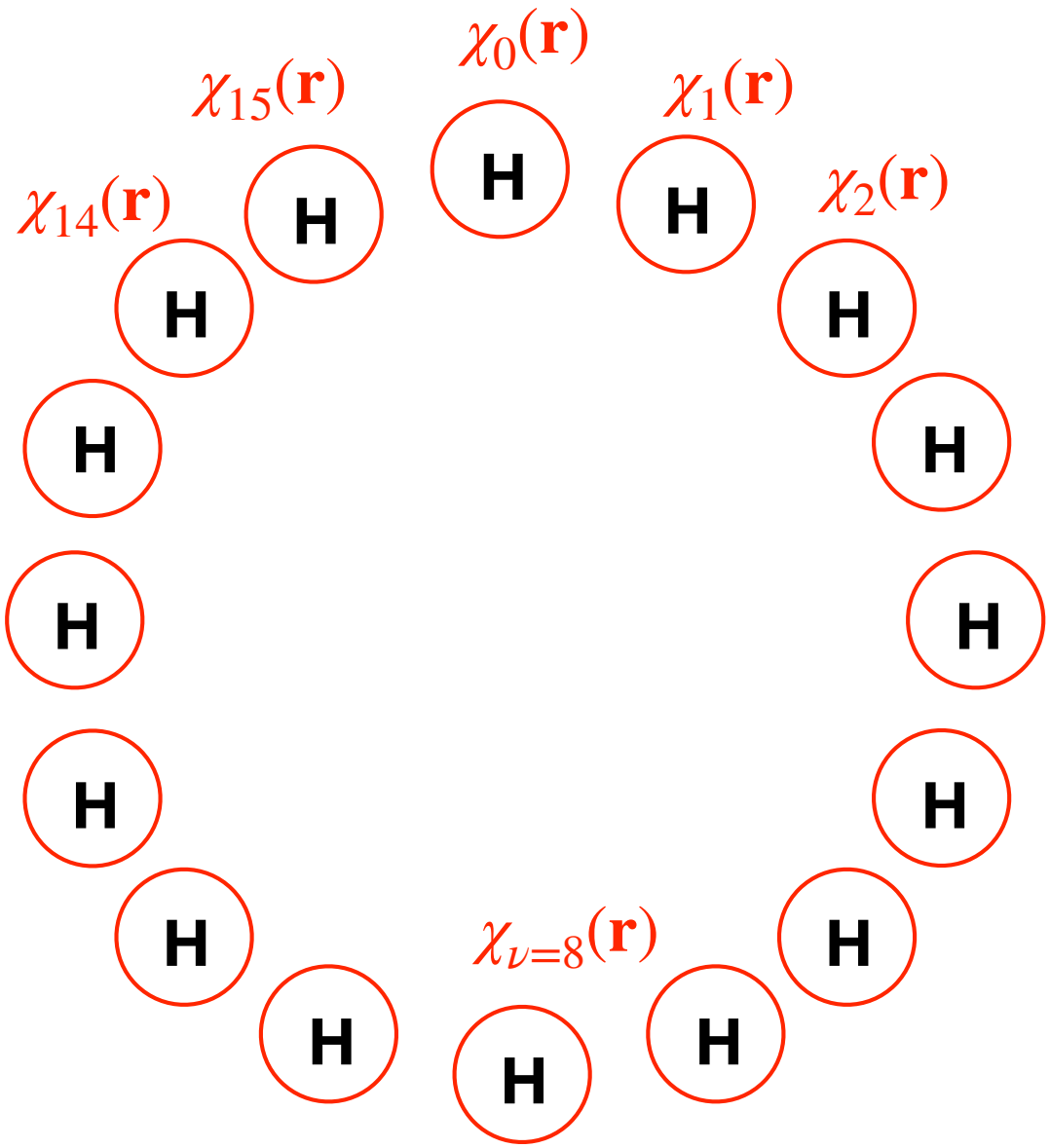
Prototypical ring of $L = 16$ hydrogen atoms



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

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*

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

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

One-electron integrals

Schrödinger equation in second quantization

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

***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*

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

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

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

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

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

Schrödinger equation in second quantization

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

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*

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

Slater determinant

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*

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

Configuration Interaction (CI) coefficient

Configuration interaction (CI) method

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

Slater determinant

CI coefficient

Configuration interaction (CI) method

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

CI coefficient

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

Configuration interaction (CI) method

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

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

Known

Configuration interaction (CI) method

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

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

Orthonormal basis of N-electron states

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

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***

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

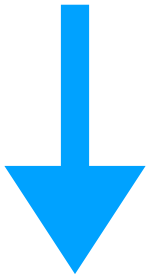
Proof:

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

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

Proof:

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



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

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

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

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:

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

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

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

Proof:

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

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

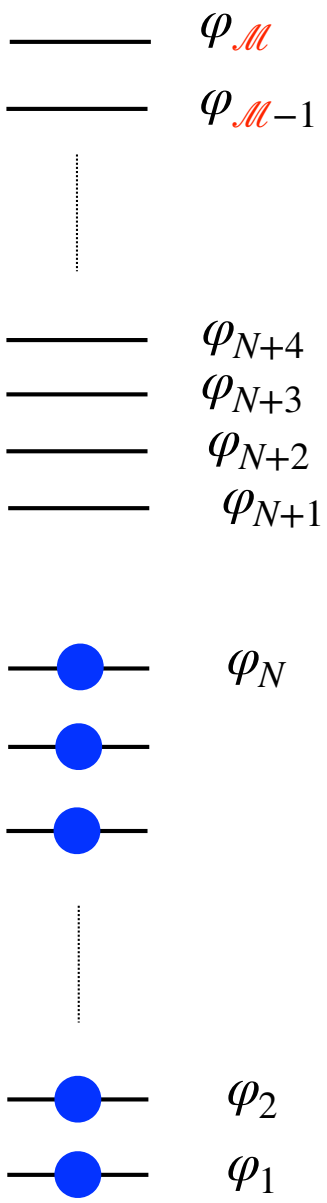
Proof:

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

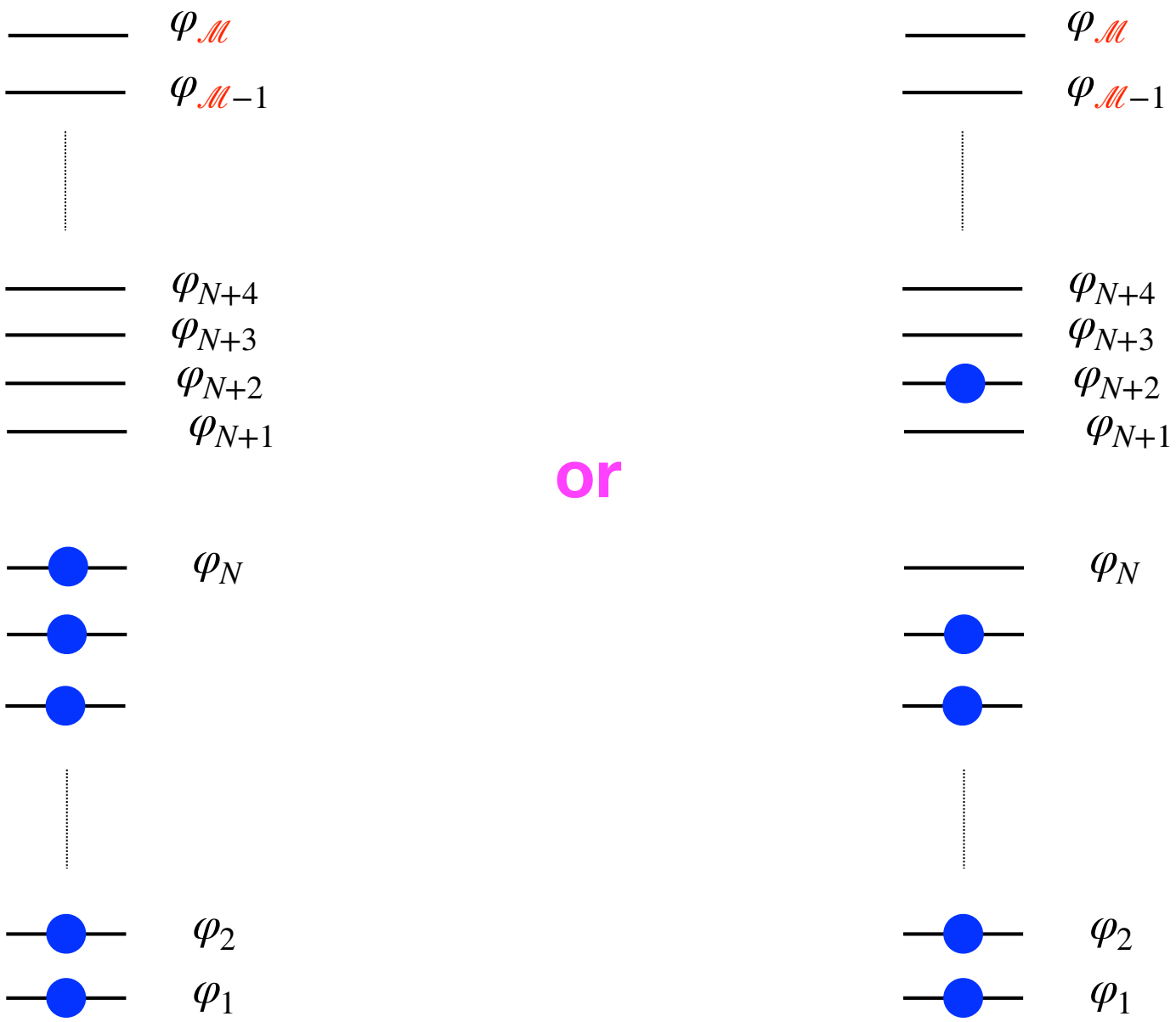
$$\mathbf{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{\mathscr{I}} \\ \vdots \end{bmatrix} \quad \Updownarrow$$

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

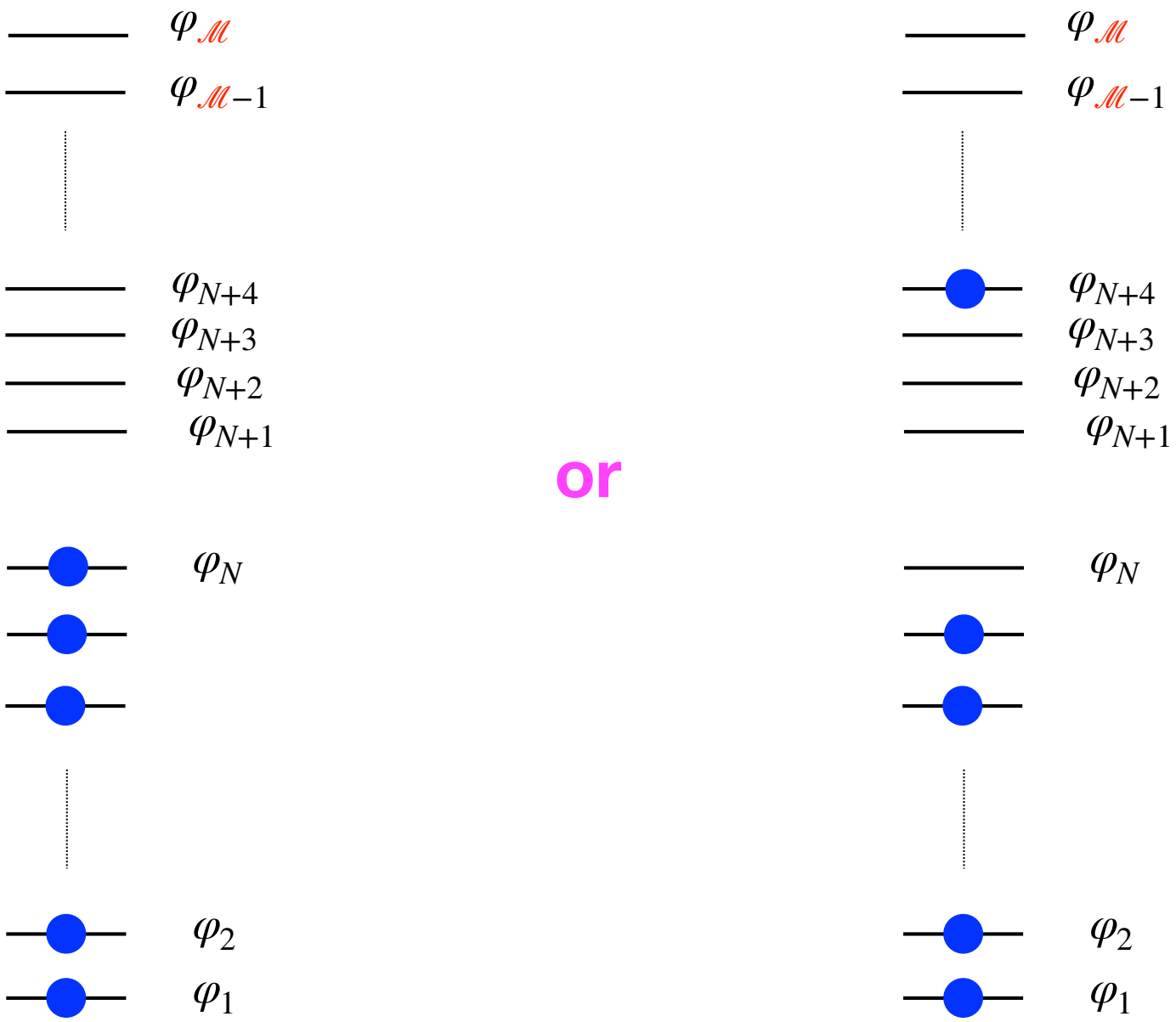
How many determinants in total?



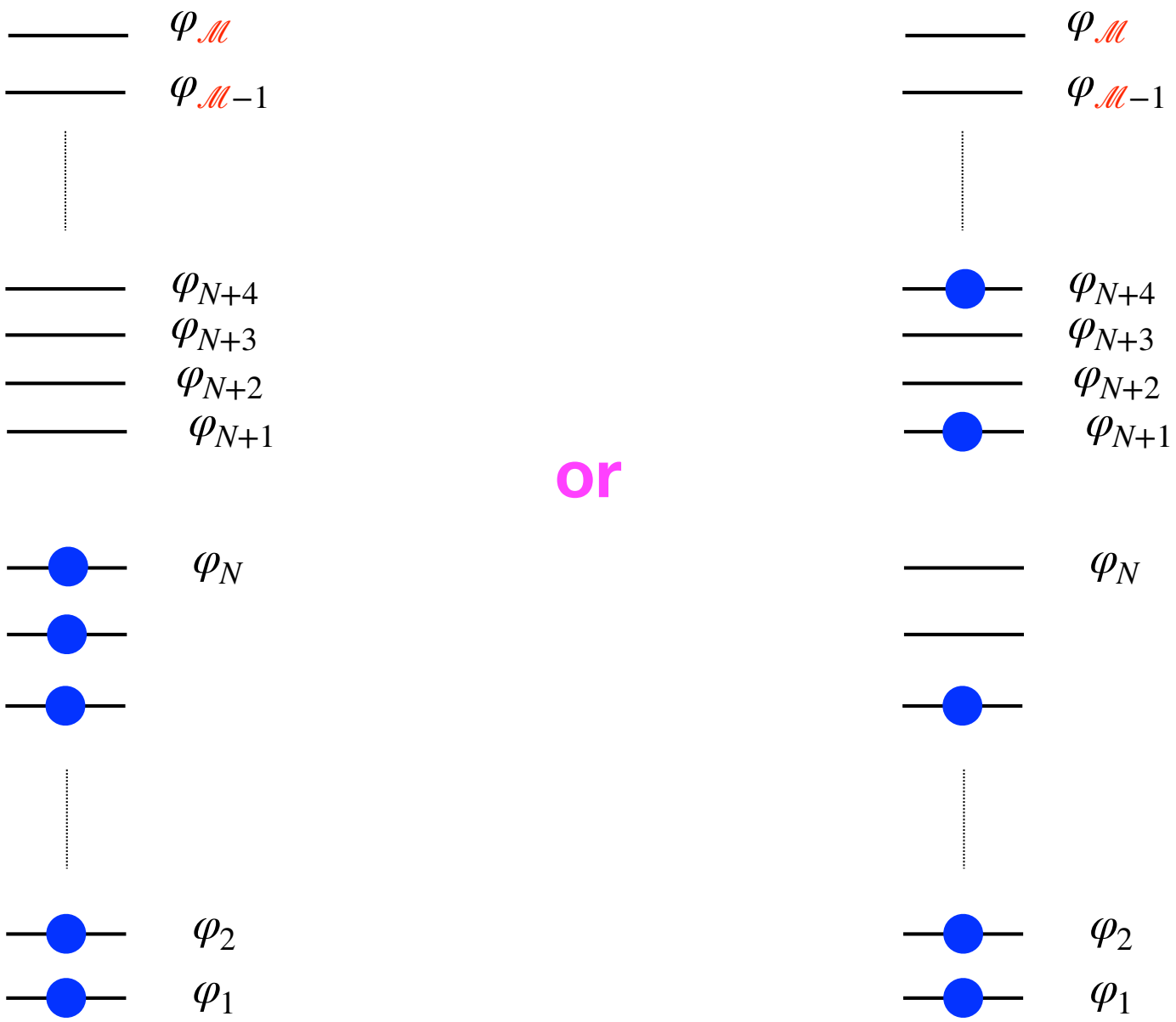
How many determinants in total?



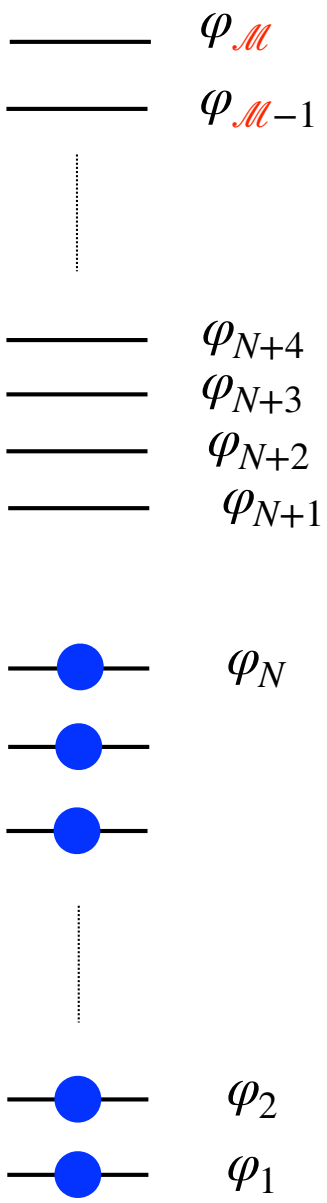
How many determinants in total?



How many determinants in total?



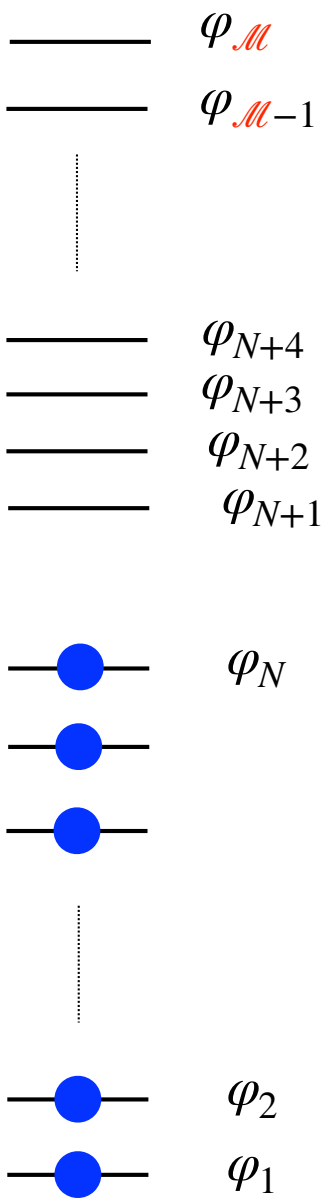
How many determinants in total?



or

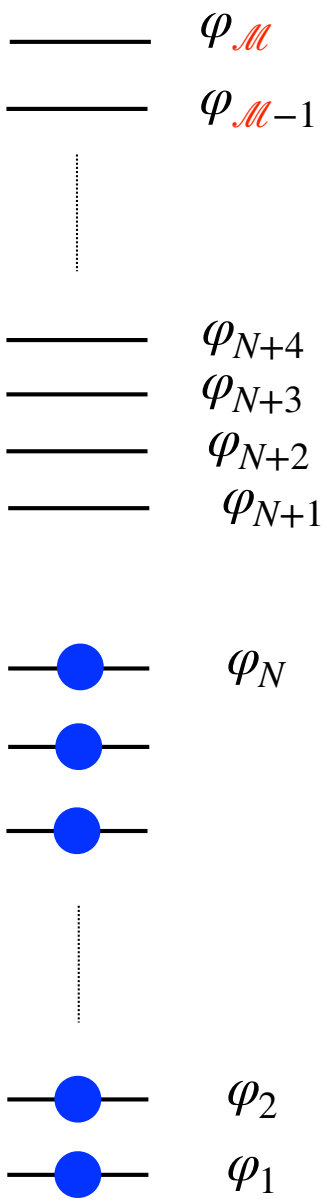
Etc…

How many determinants in total?



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

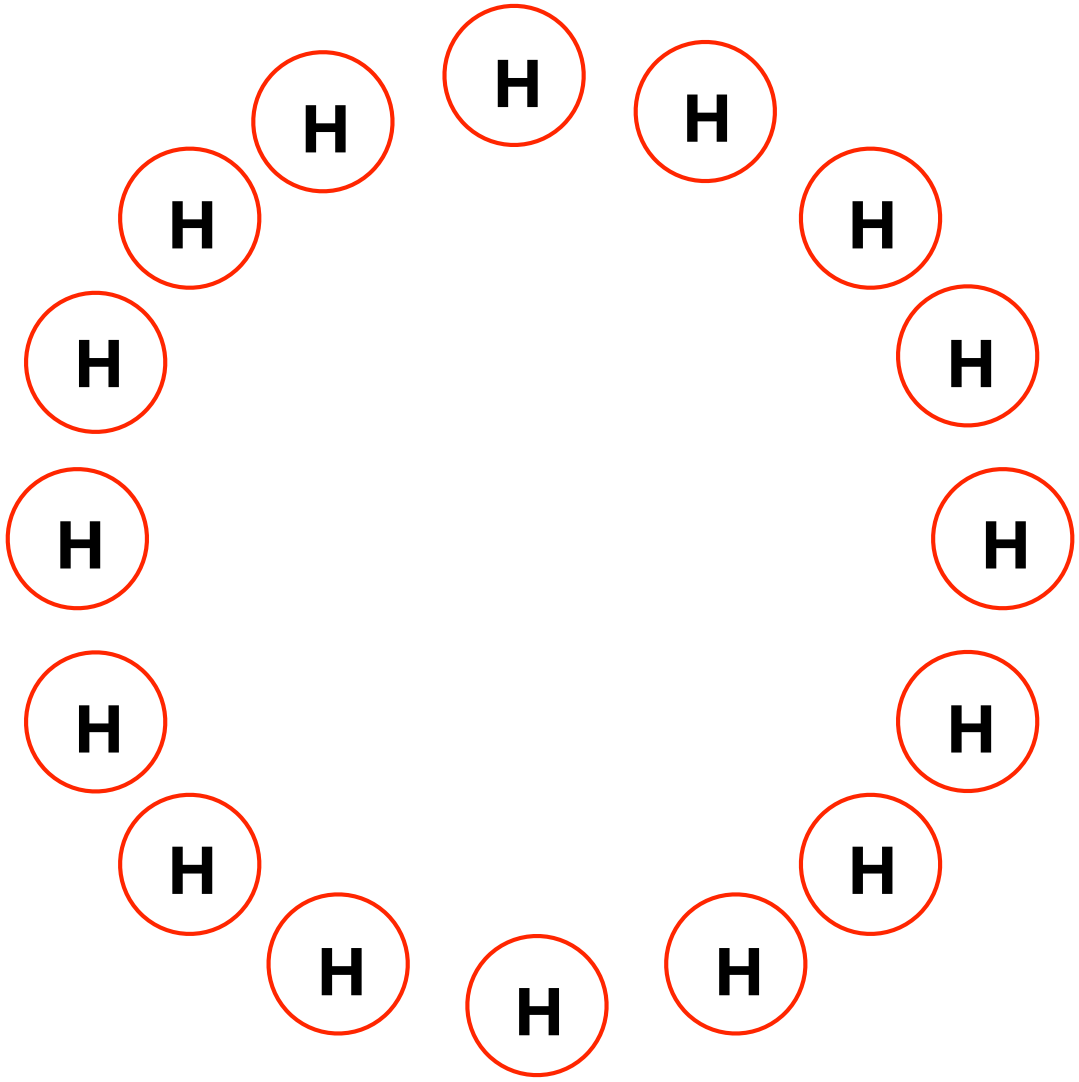
How many determinants in total?



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"

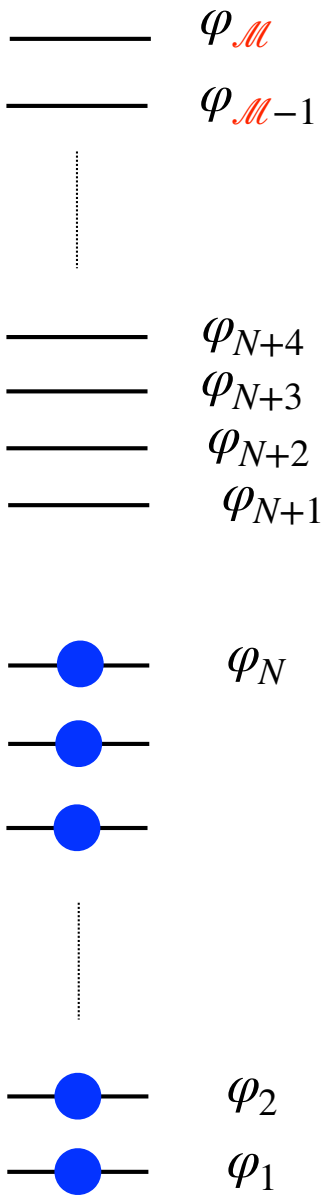
How many determinants in total?

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

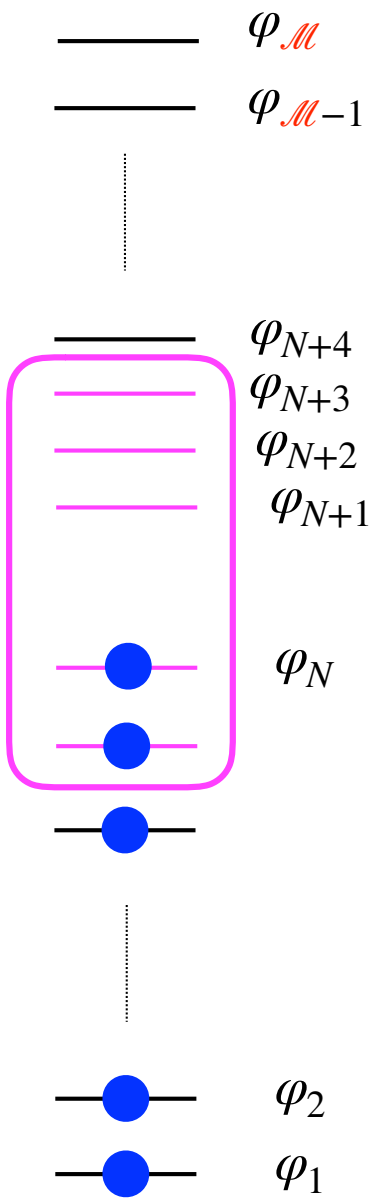
How many determinants in total?

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

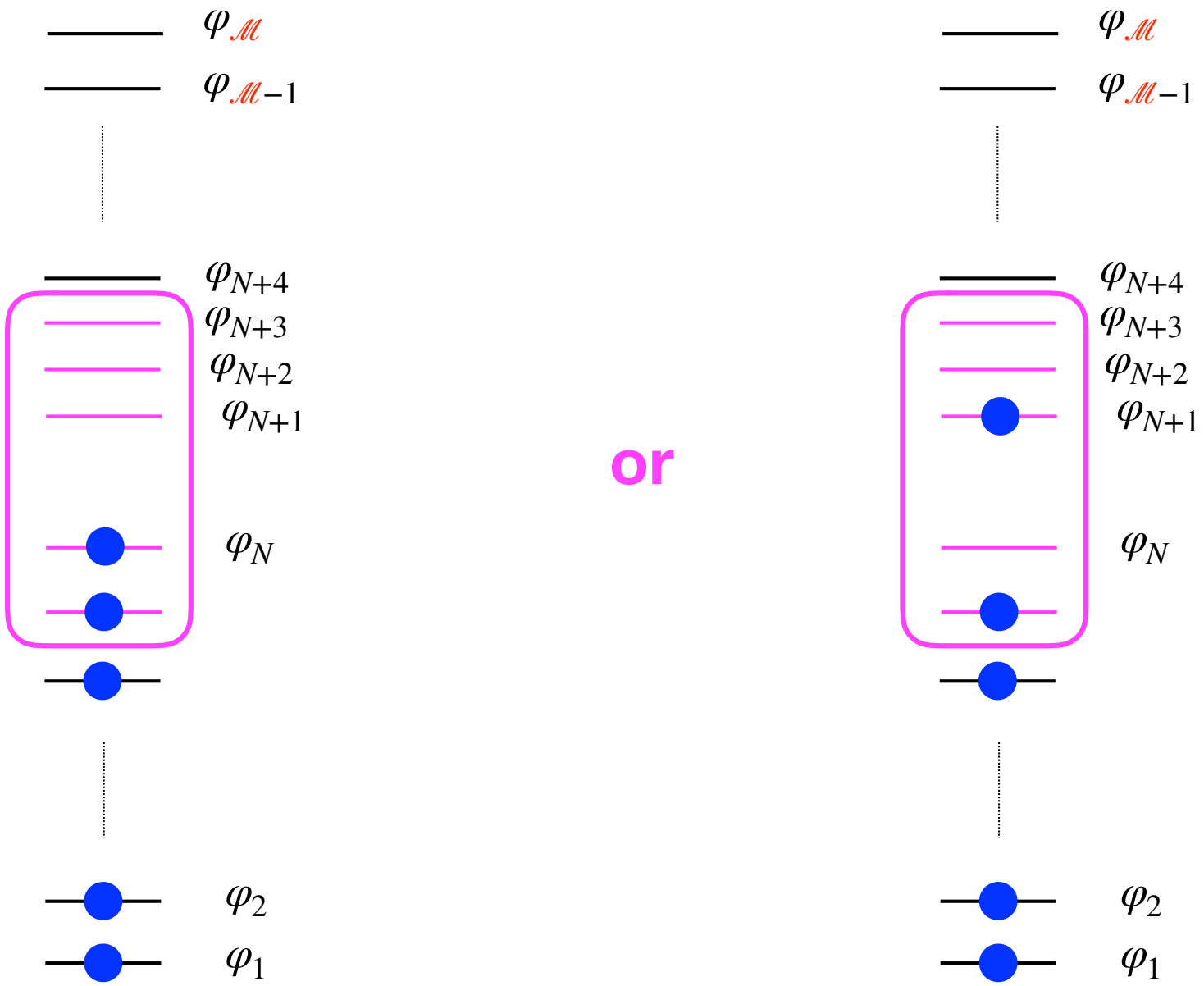
Complete active space CI (CAS-CI) method



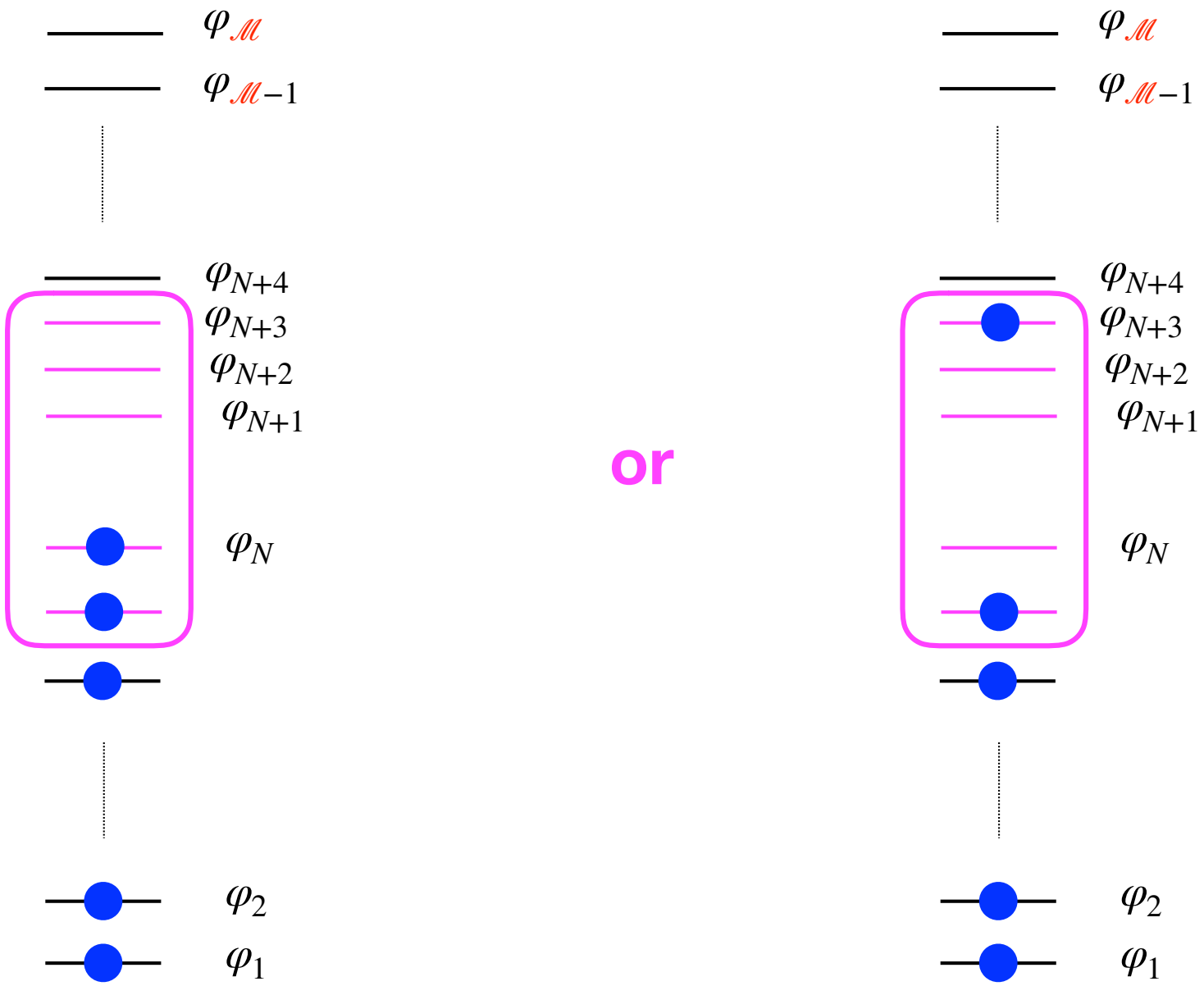
Complete active space CI (CAS-CI) method



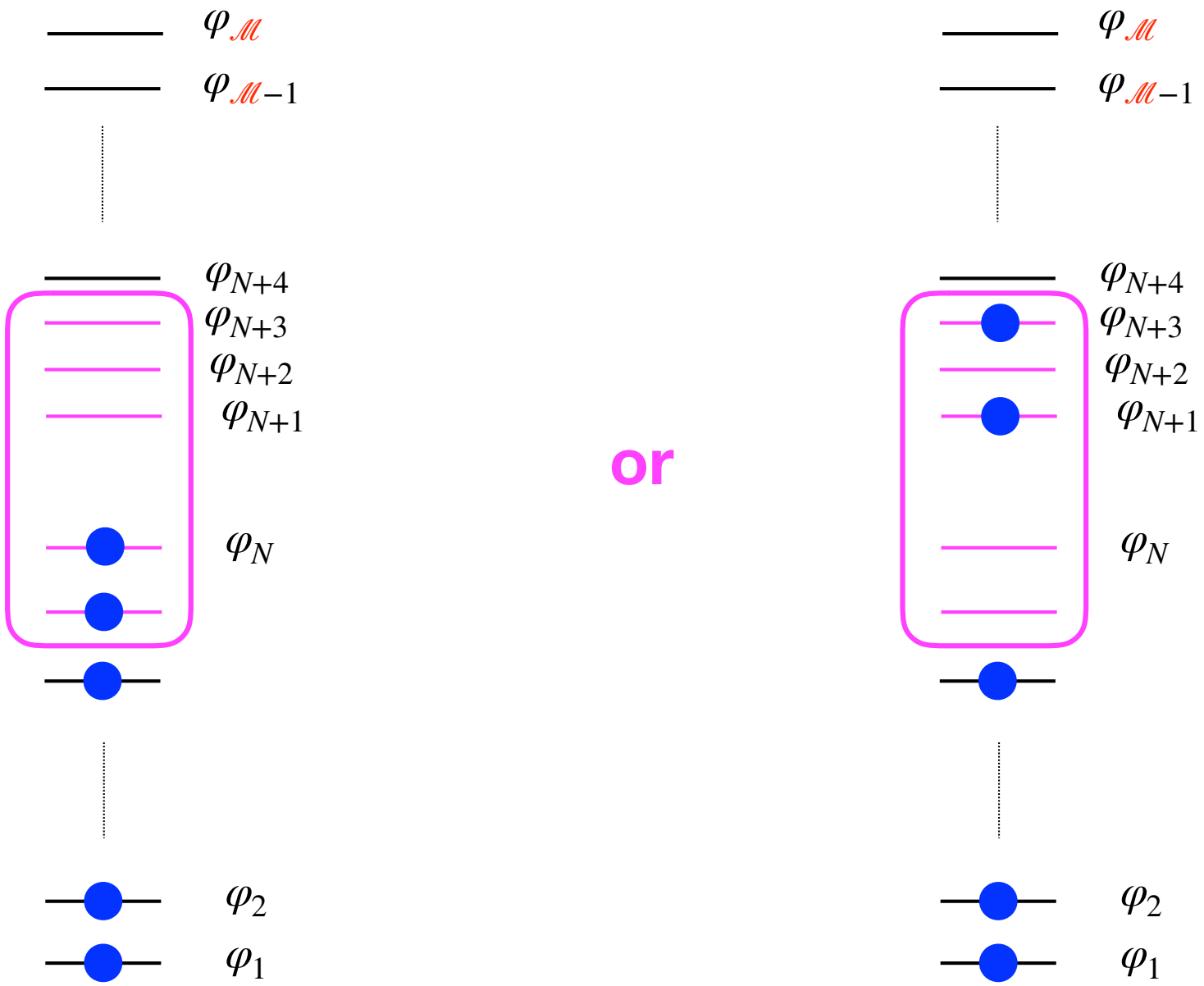
Complete active space CI (CAS-CI) method



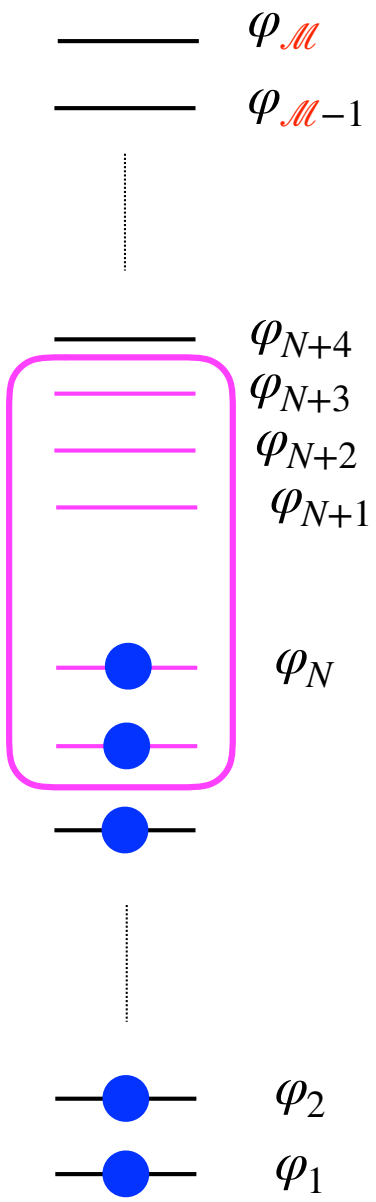
Complete active space CI (CAS-CI) method



Complete active space CI (CAS-CI) method

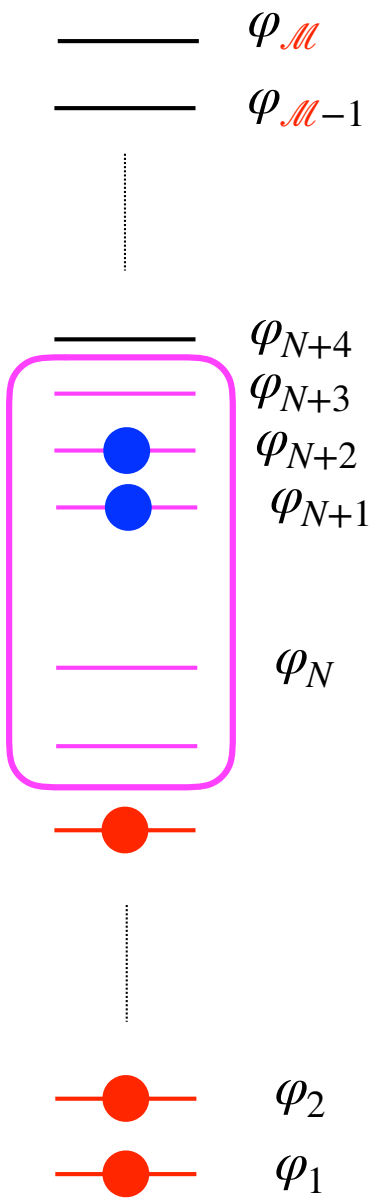


Complete active space CI (CAS-CI) method



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

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

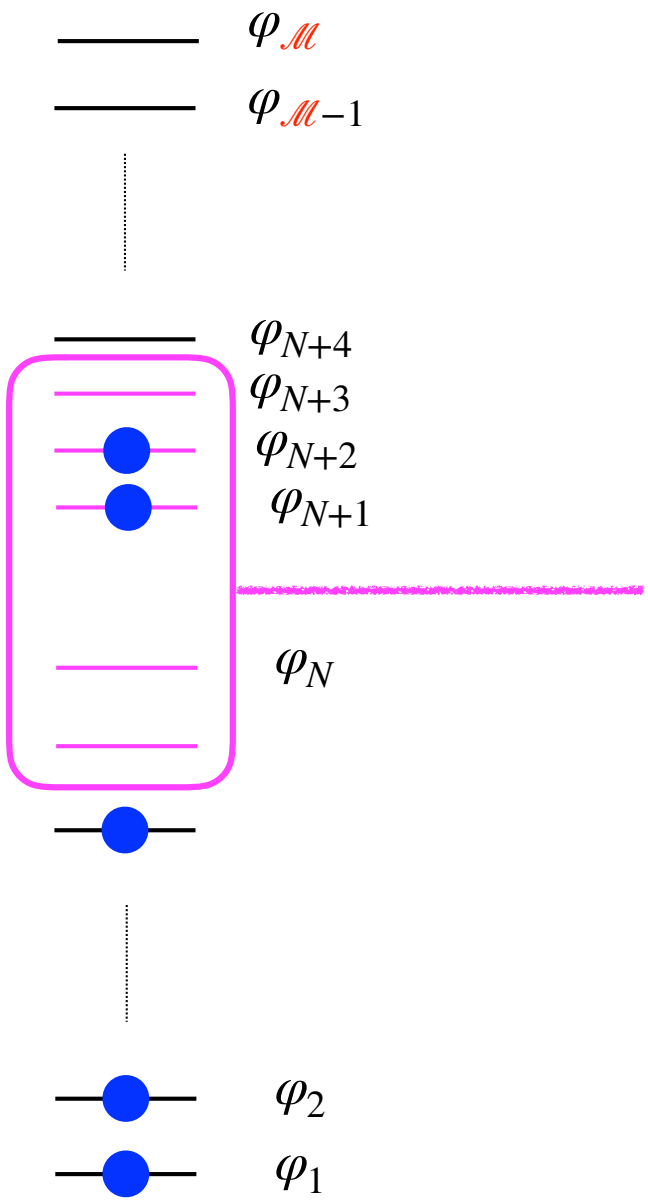
"resolution of the identity"

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

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

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

Effective Hamiltonian

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

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

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

Effective Hamiltonian

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

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

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***

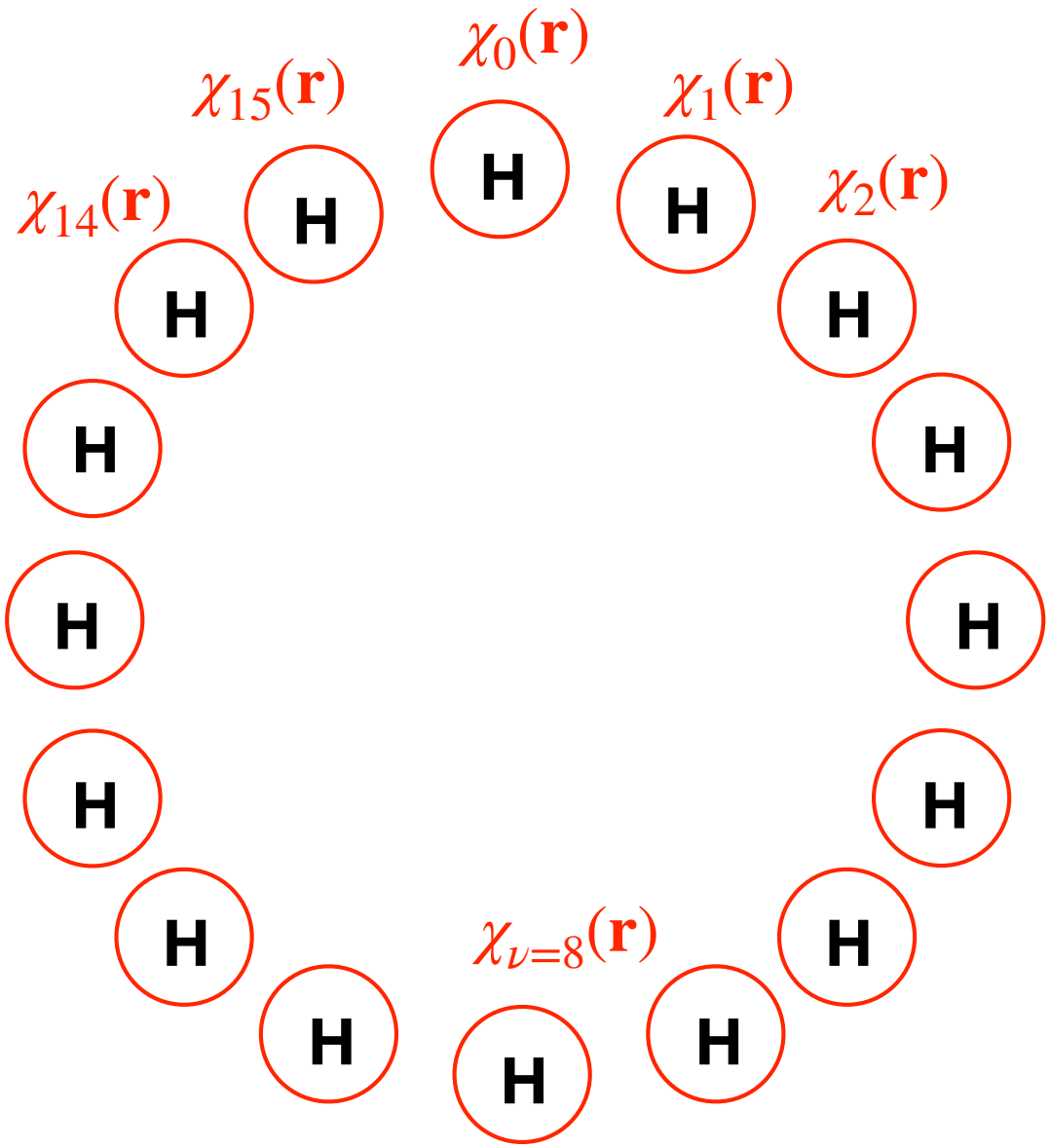
$$\hat{H}_{\text{eff}}(E) = \hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\left[E\hat{Q} - \hat{Q}\hat{H}\hat{Q}\right]^{-1}\hat{Q}\hat{H}\hat{P}$$

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

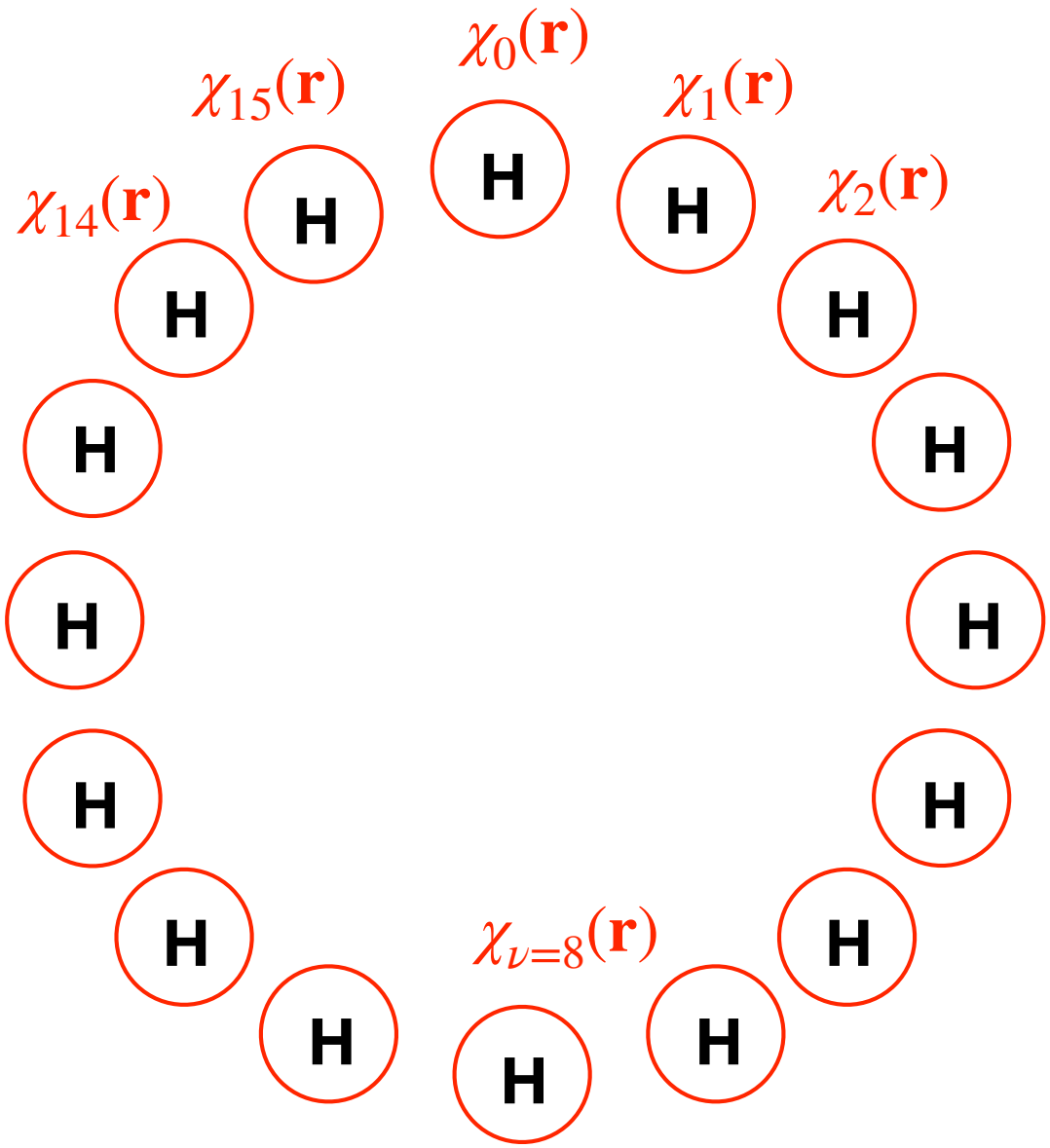


Molecular spin-orbitals

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

Delocalised over the ring

Prototypical ring of $L = 16$ hydrogen atoms



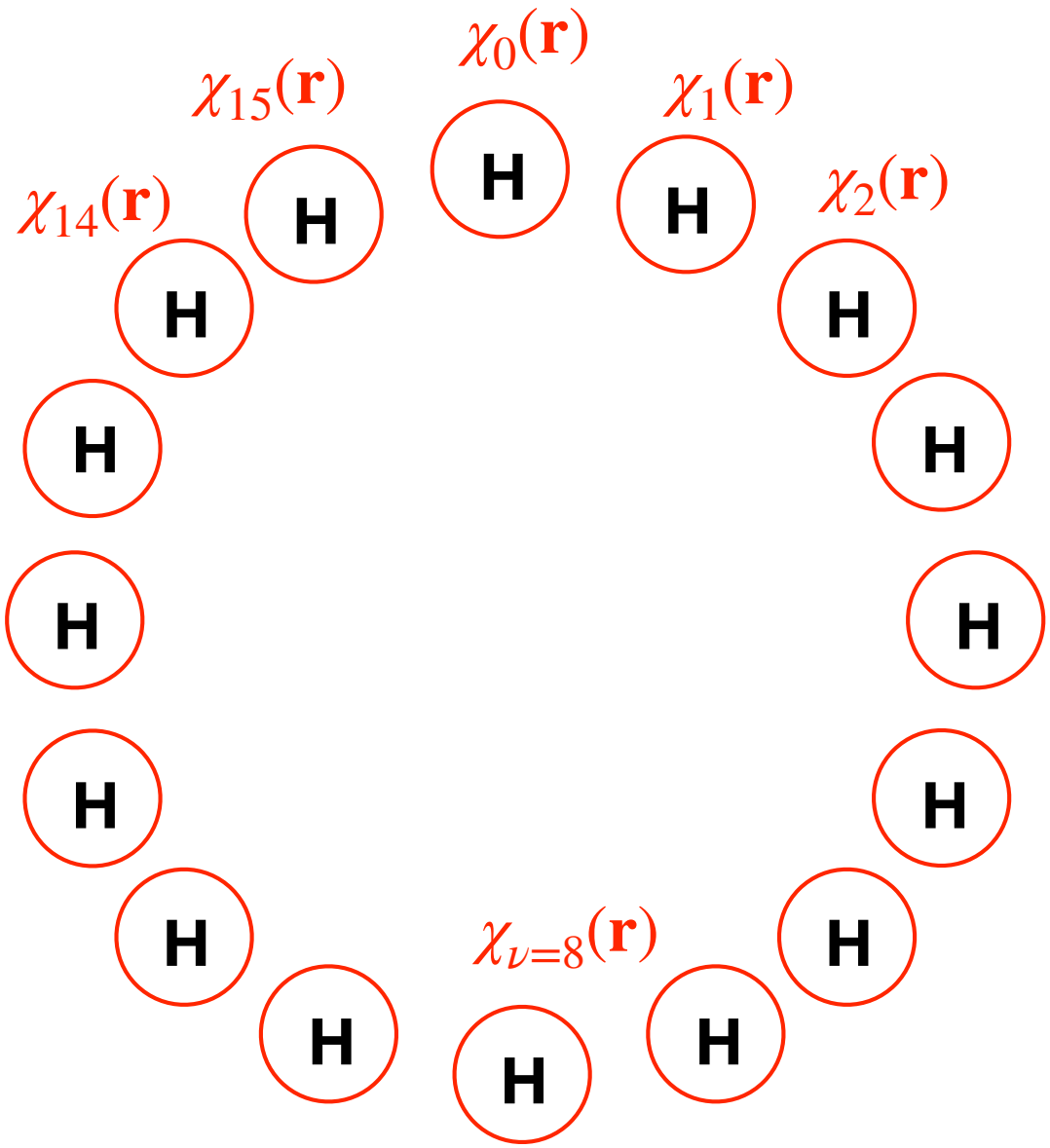
Delocalized molecular spin-orbitals

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

Dirac notation

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

Prototypical ring of $L = 16$ hydrogen atoms



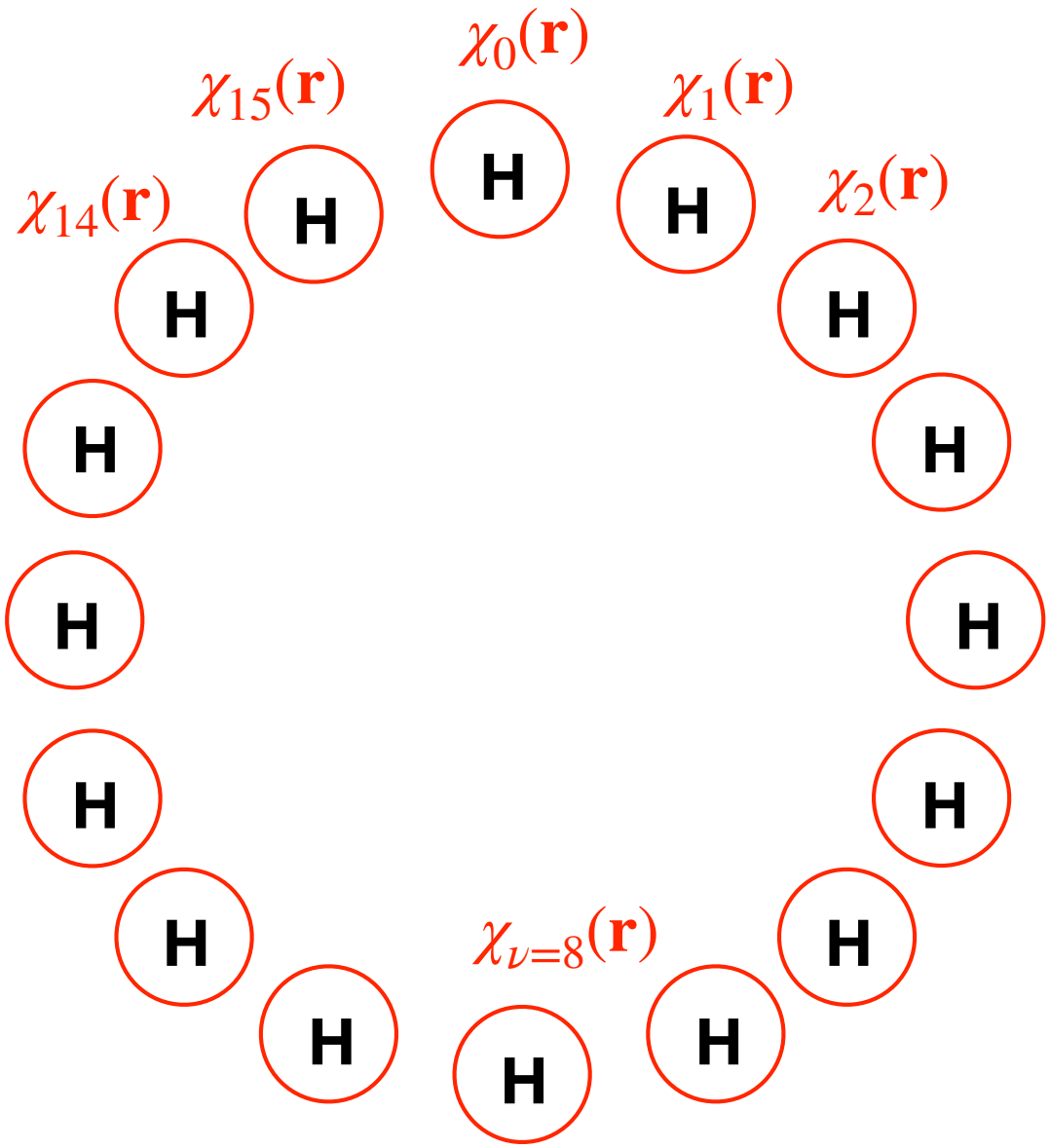
Delocalized molecular spin-orbitals

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

Second-quantized notation

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

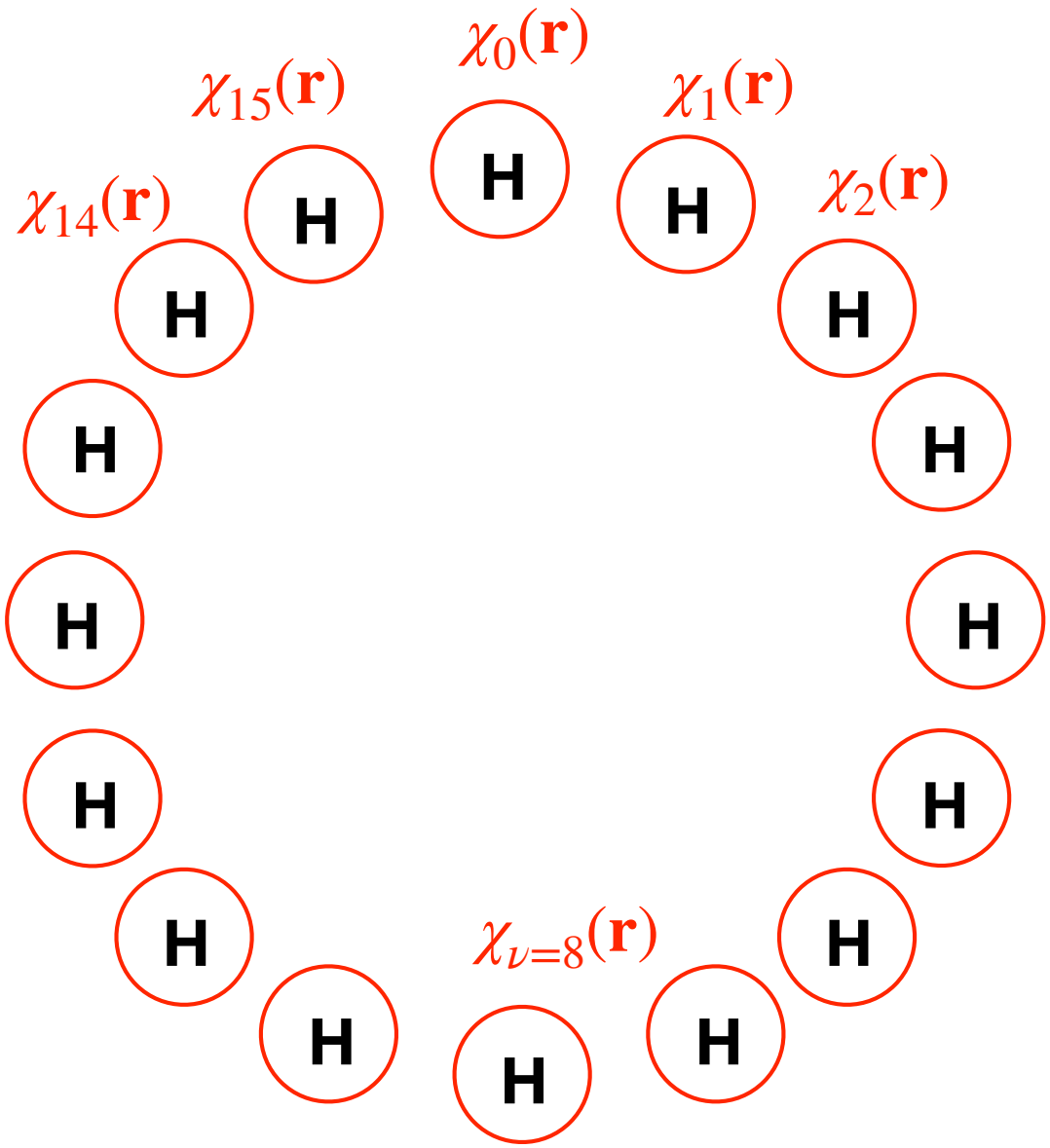
Prototypical ring of $L = 16$ hydrogen atoms



*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

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

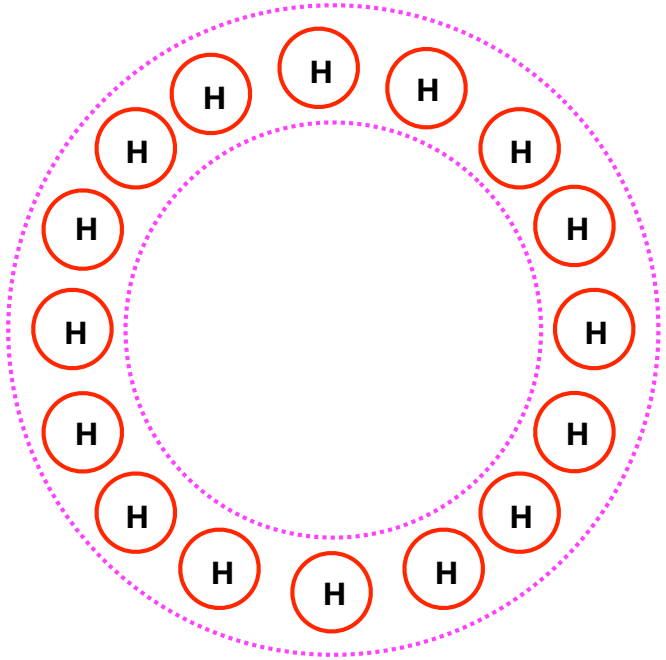
Change of representation in second quantization

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

Change of representation in second quantization

*Chemist's **delocalized** representation*

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

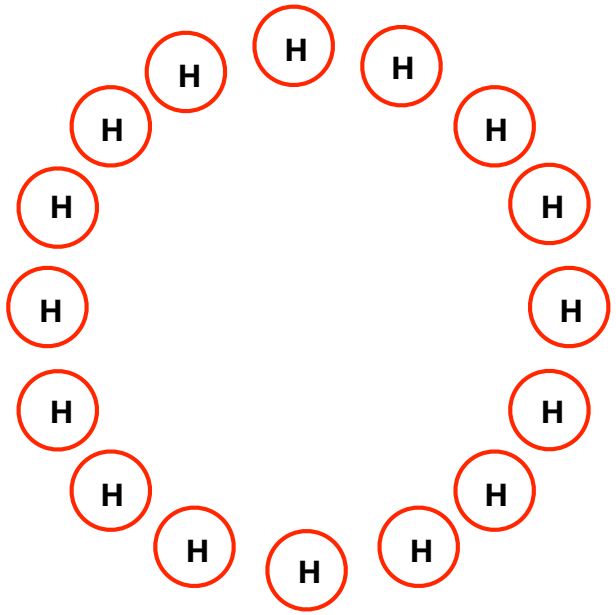


$$\varphi_P(\mathbf{x}) = \sum_\nu C_{\nu P}\, \chi_\nu(\mathbf{x})$$

Change of representation in second quantization

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

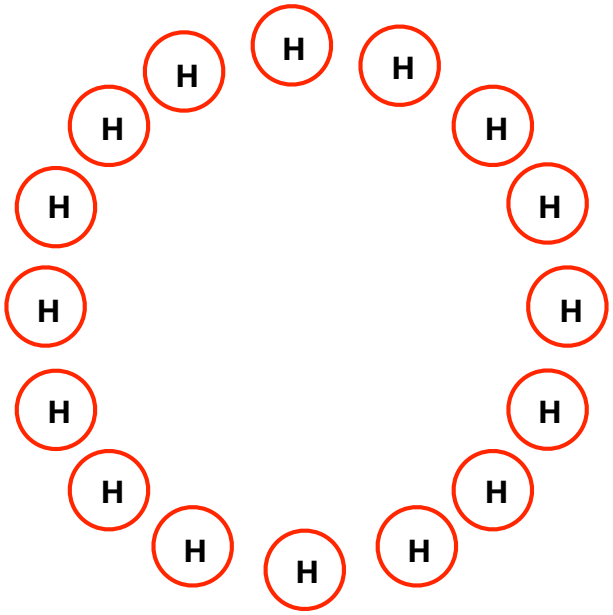
→ *Physicist's **localized** representation*



Change of representation in second quantization

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

*Physicist's **localized** representation*

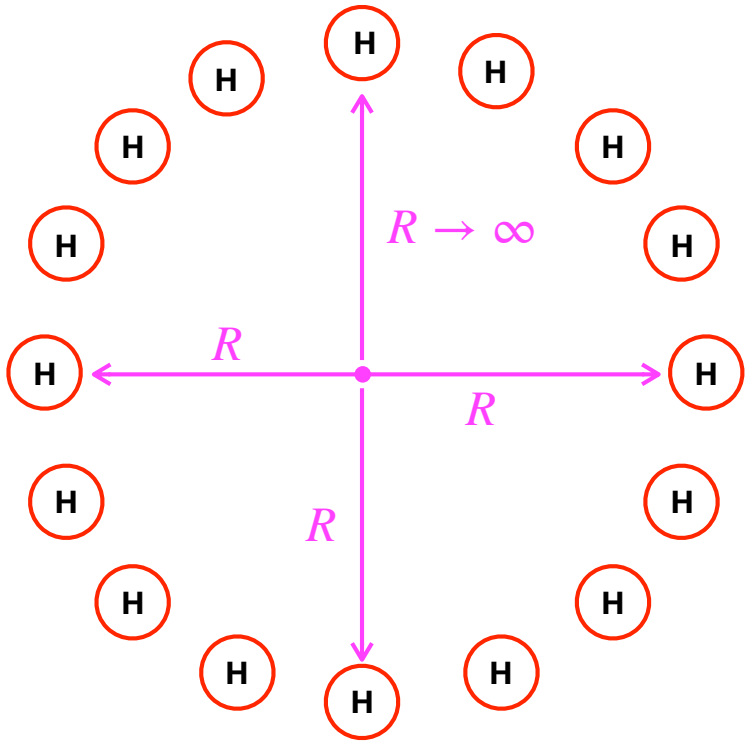


*Allows for a **fragmentation** of the molecule in the orbital space!*

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*

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

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

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

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

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

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

One-electron integrals in the localised orbital basis

Hamiltonian in the localised representation

Delocalized *representation*

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

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

Localized *representation*

Hamiltonian in the localised representation

Delocalized *representation*

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

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

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

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

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

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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

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

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One-electron reduced density matrix (1RDM)

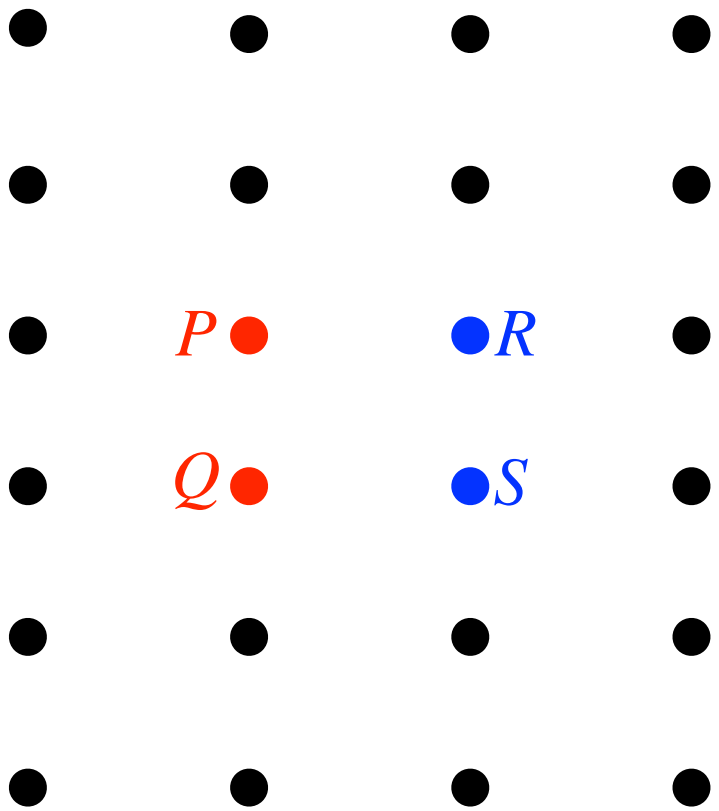
Two-electron reduced density matrix (2RDM)

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

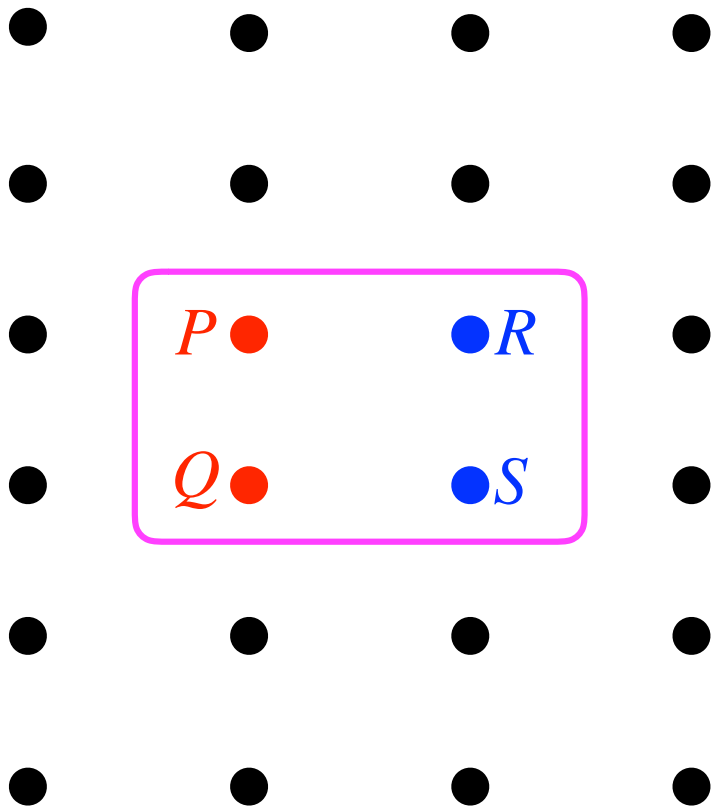
$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

Reduced density matrices

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



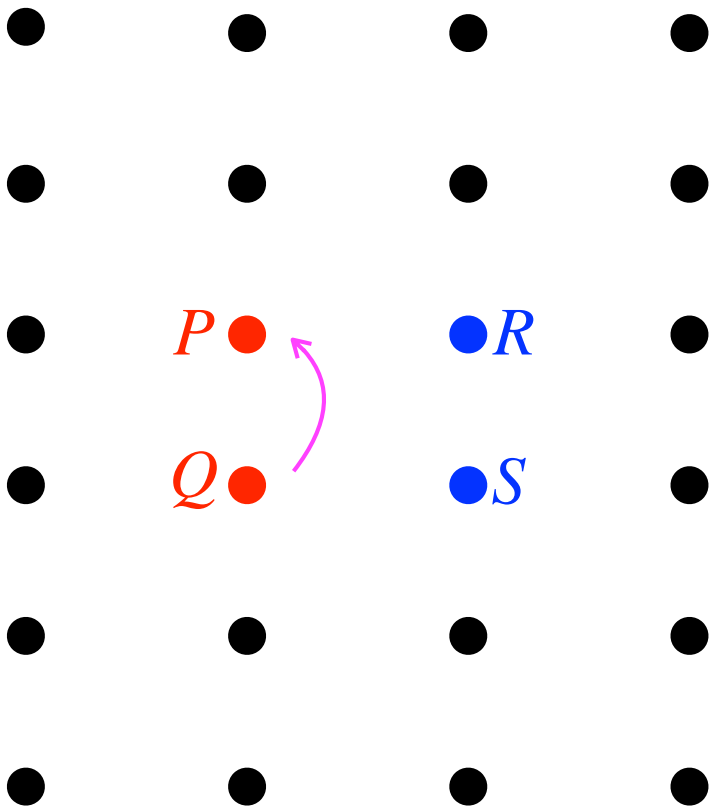
Reduced density matrices



"fragment"

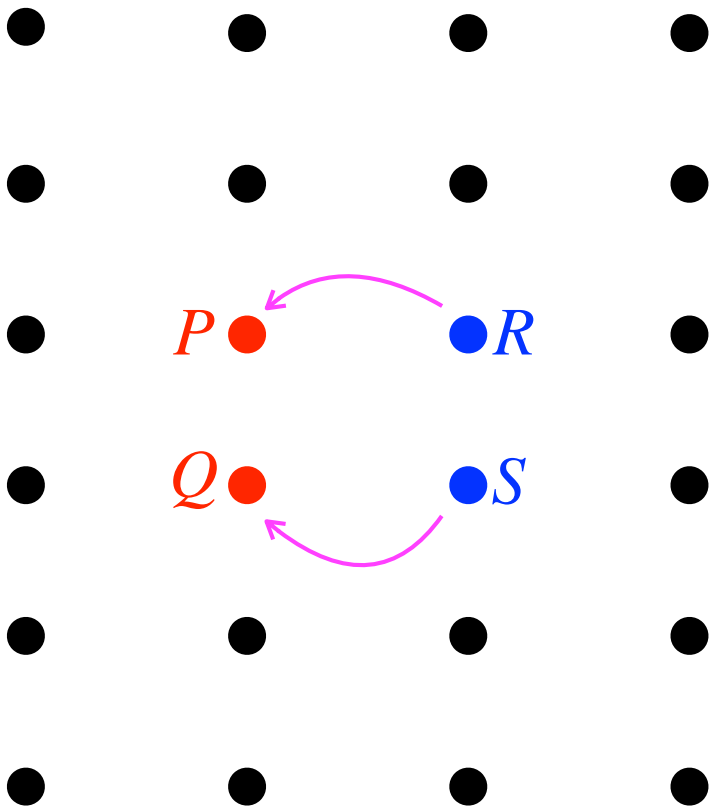
Reduced density matrices

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



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

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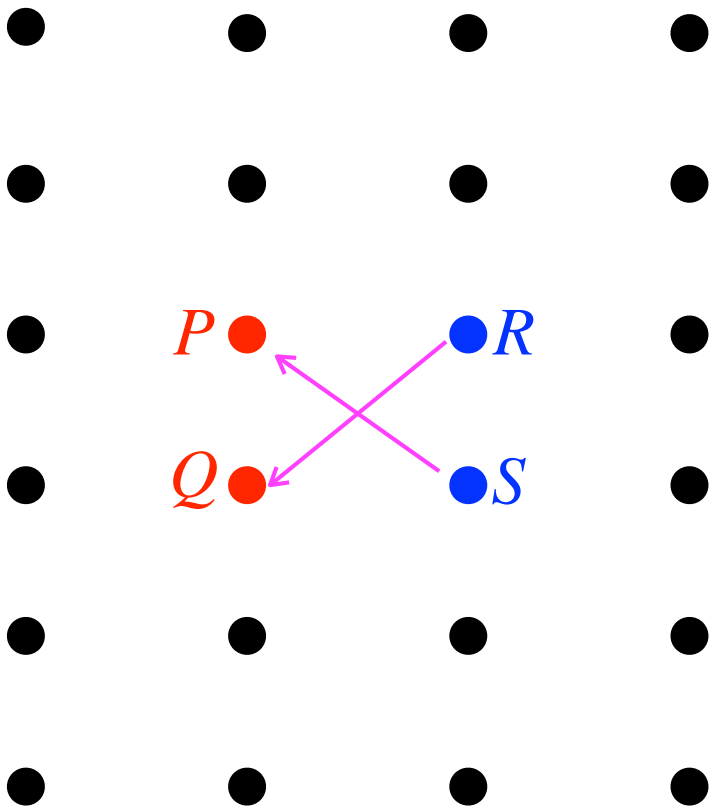
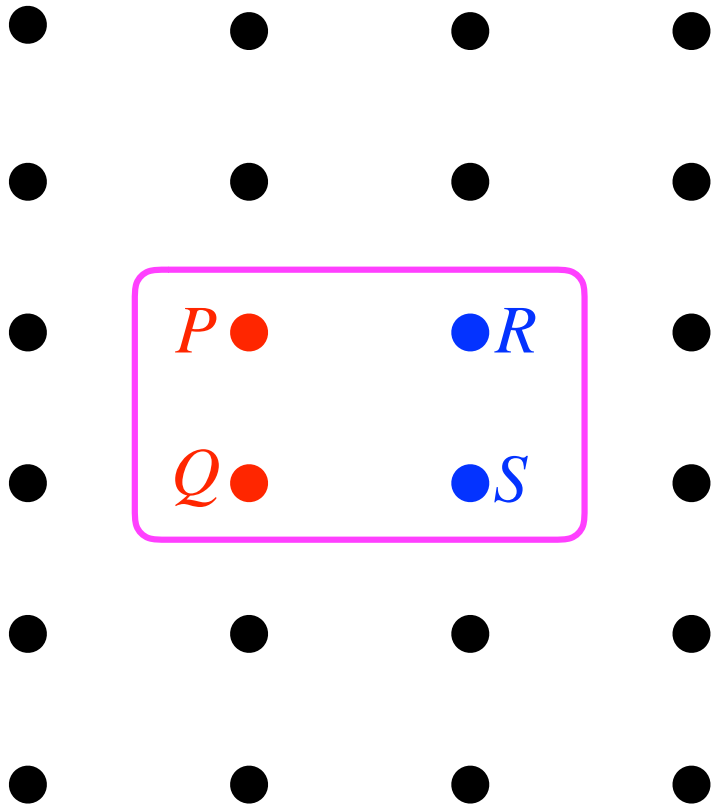


Reduced density matrices

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



Reduced density matrices

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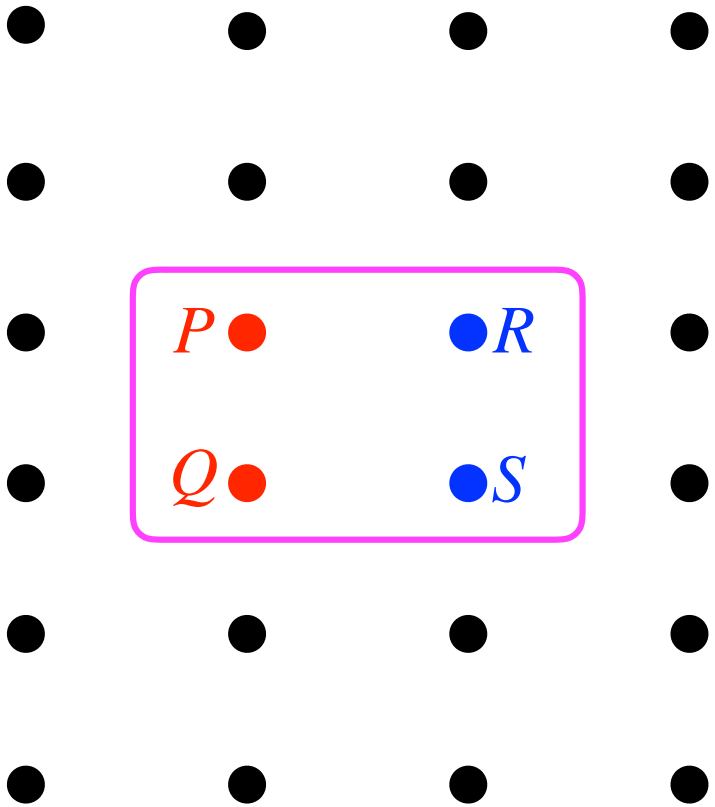
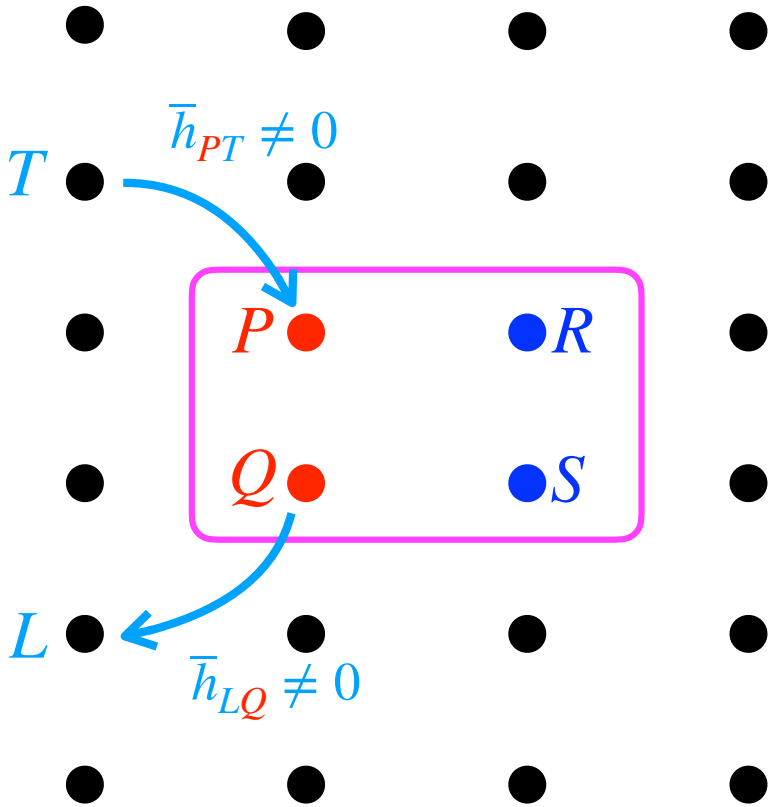


Open quantum subsystem

Reduced density matrices

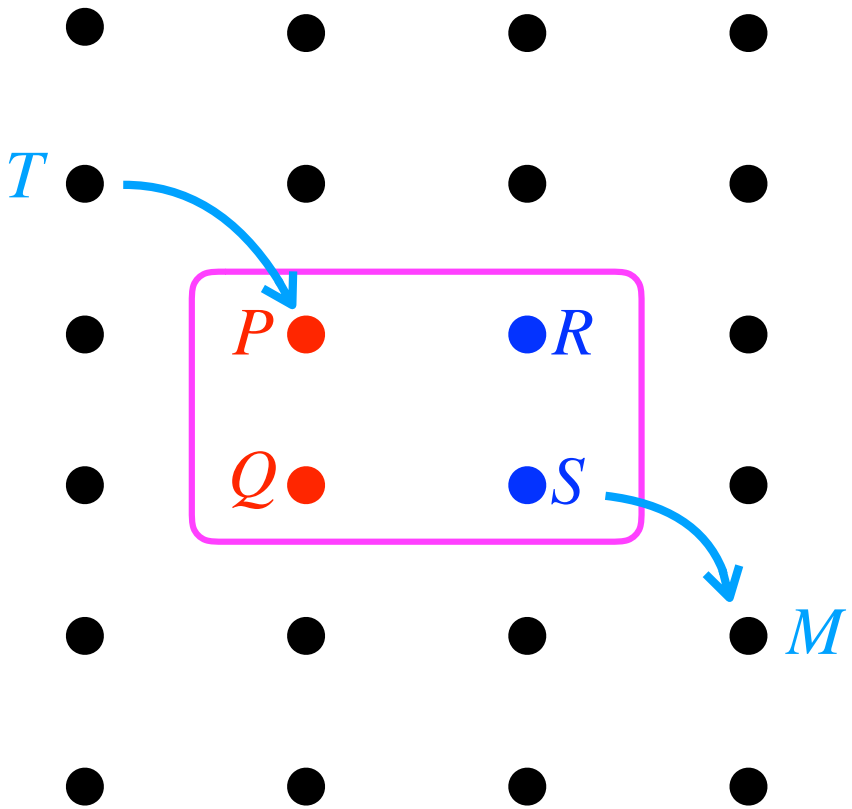
$$\hat{H} \equiv \sum_{PQ} \bar{h}_{PQ}\, \hat{c}_P^\dagger \hat{c}_Q + \frac{1}{2} \sum_{PQRS} \bar{g}_{PQRS}\, \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R$$



Entanglement

Reduced density matrices

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



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

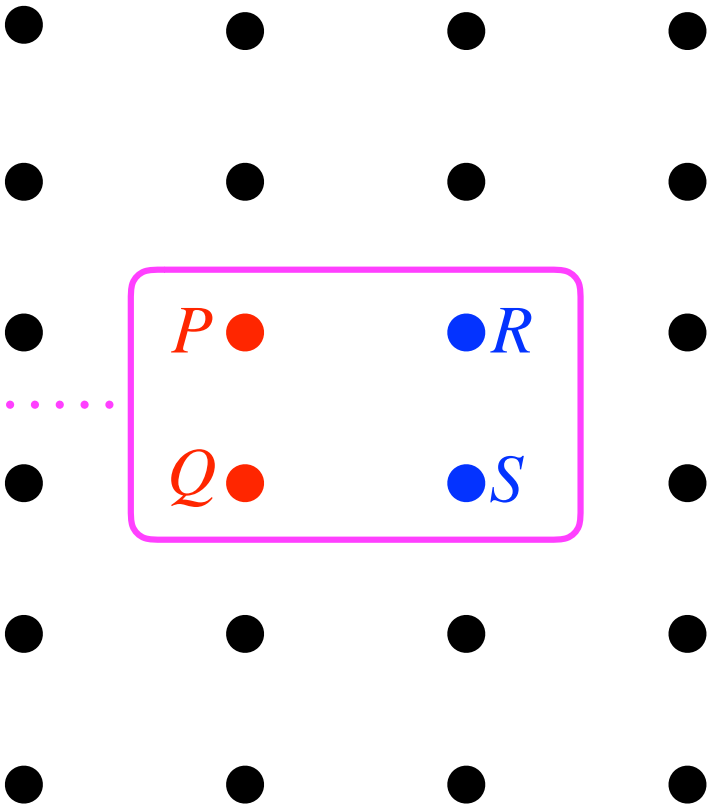
Entanglement

Reduced density matrices

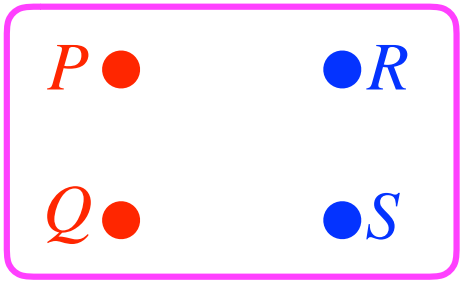
The evaluation of the RDMs requires, in principle, the ***full wave function*** Ψ_0

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

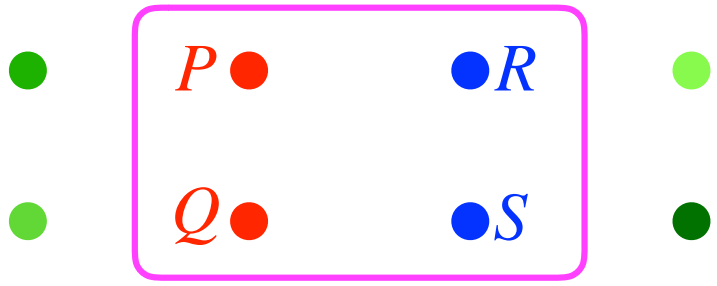
$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$



Embedding of localised spin-orbitals

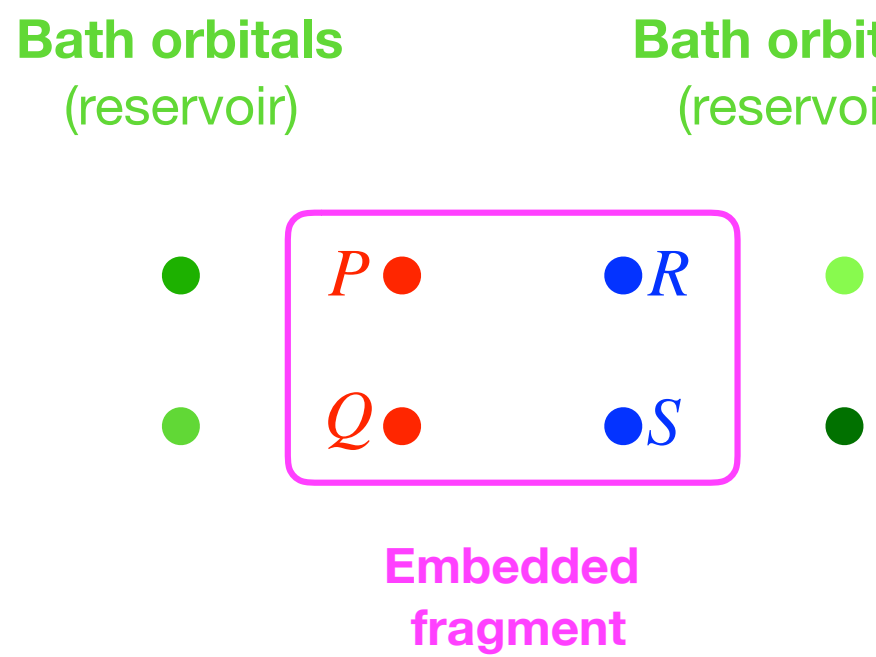


Embedding of localised spin-orbitals

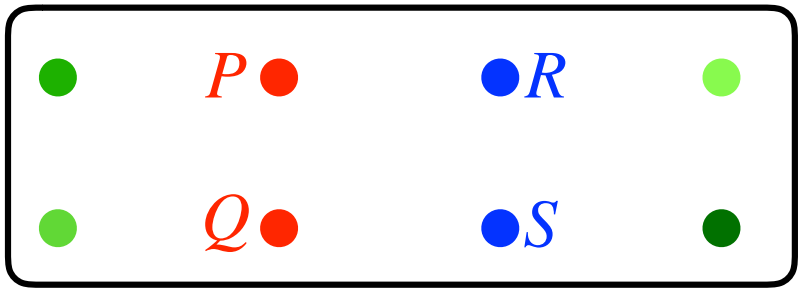


Embedding of localised spin-orbitals

Embedding of localised spin-orbitals



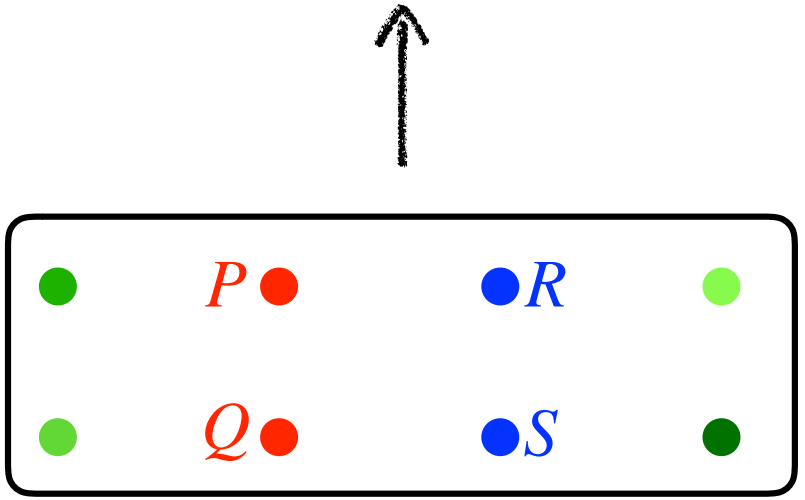
Embedding of localised spin-orbitals



Cluster

Embedding of localised spin-orbitals

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



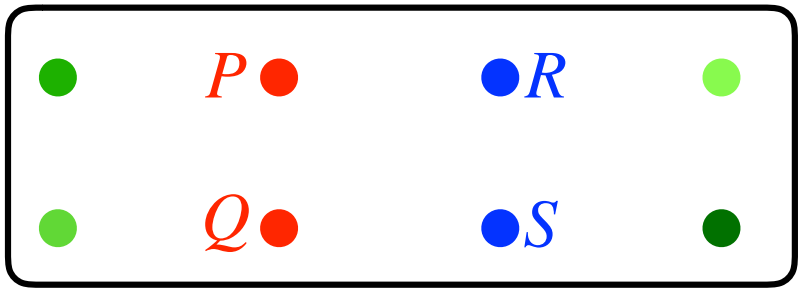
$\Psi^{\mathscr{C}}$

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