Université de Strasbourg

Institut de Chimie de Strasbourg UMR 7177

Correlated many-body wave functions in Quantum Chemistry *(part 2):*

Modelling strong electron correlation

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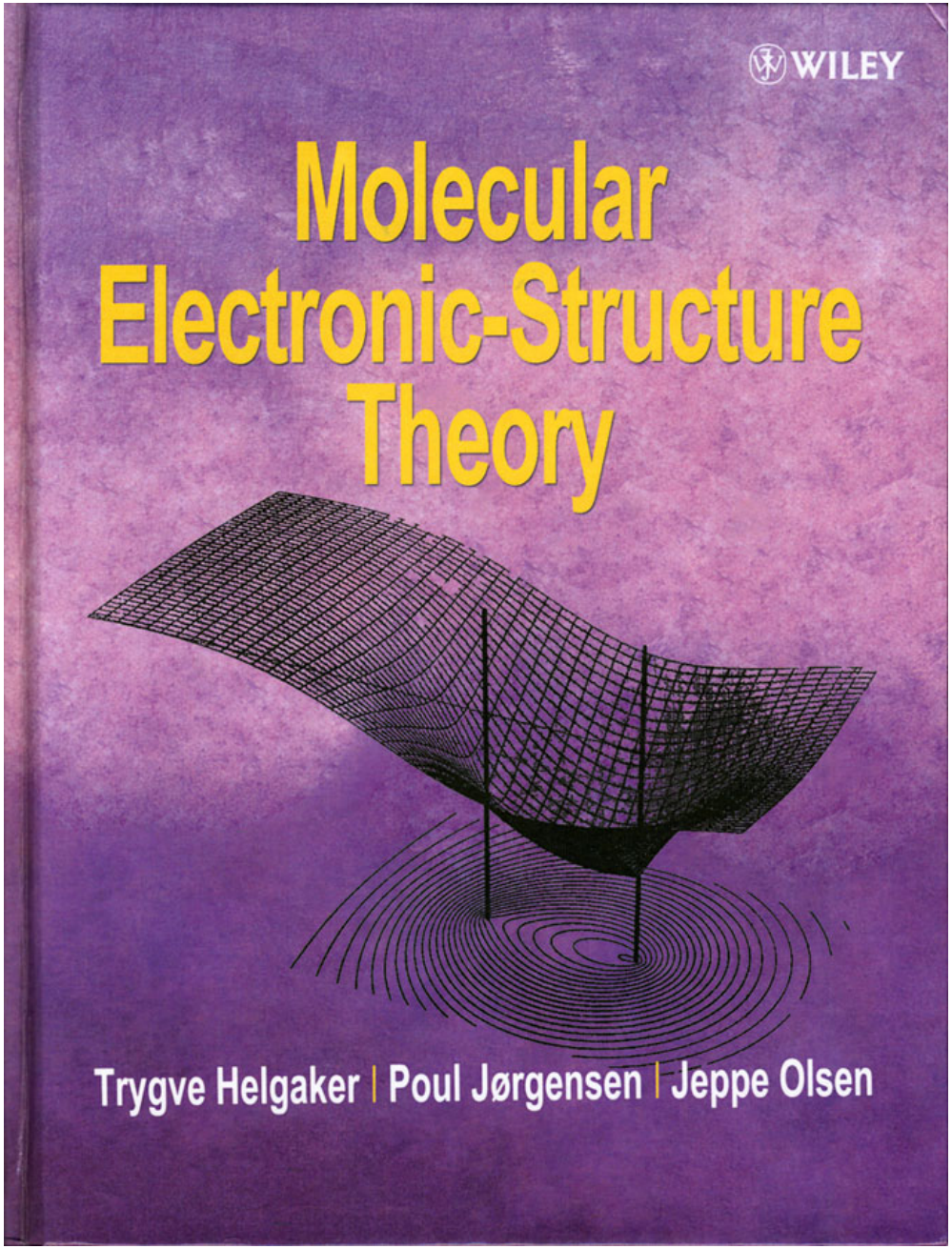
Textbook


WILEY
Molecular Electronic-Structure Theory
Trygve Helgaker | Poul Jørgensen | Jeppe Olsen

Outline

- Strong electron correlation regime

The prototypical hydrogen molecule at dissociation

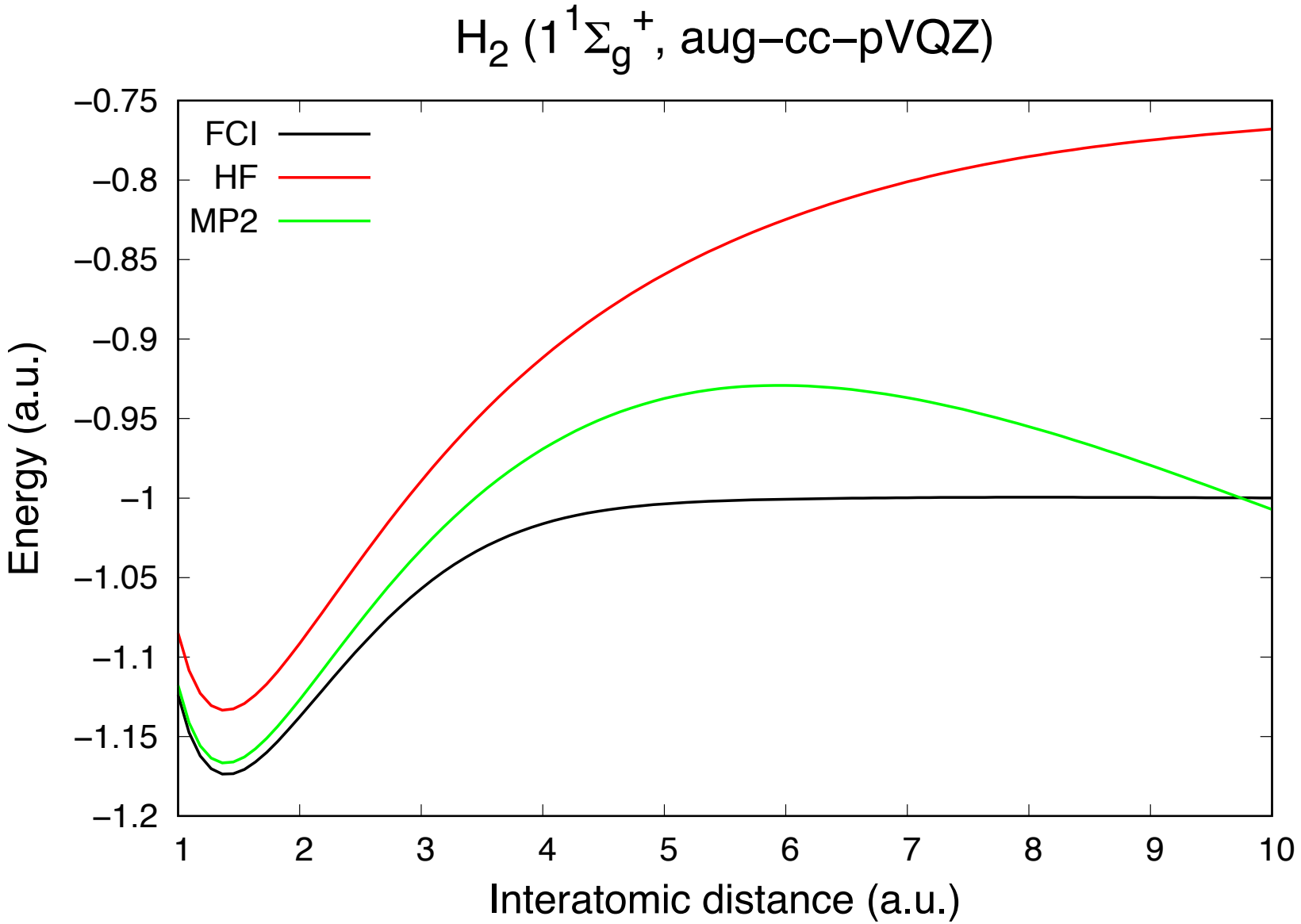
- Orbital rotation in second quantization

Orbital optimisation procedure

- **C**omplete **A**ctive **S**pace **S**elf-**C**onsistent **F**ield and beyond

General CASSCF approach, state-averaging,
multi-reference perturbation theory

Dissociation of the hydrogen molecule



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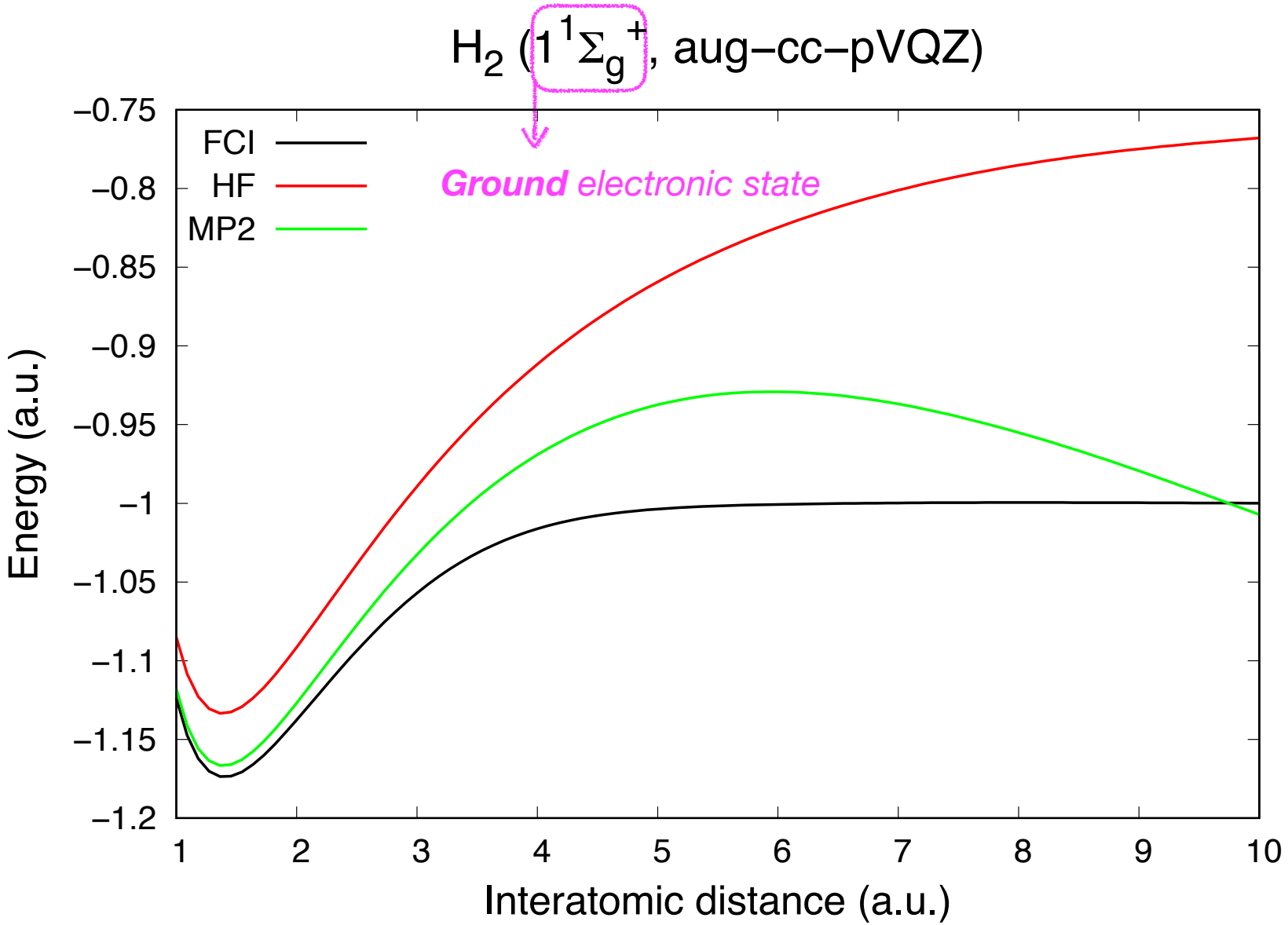

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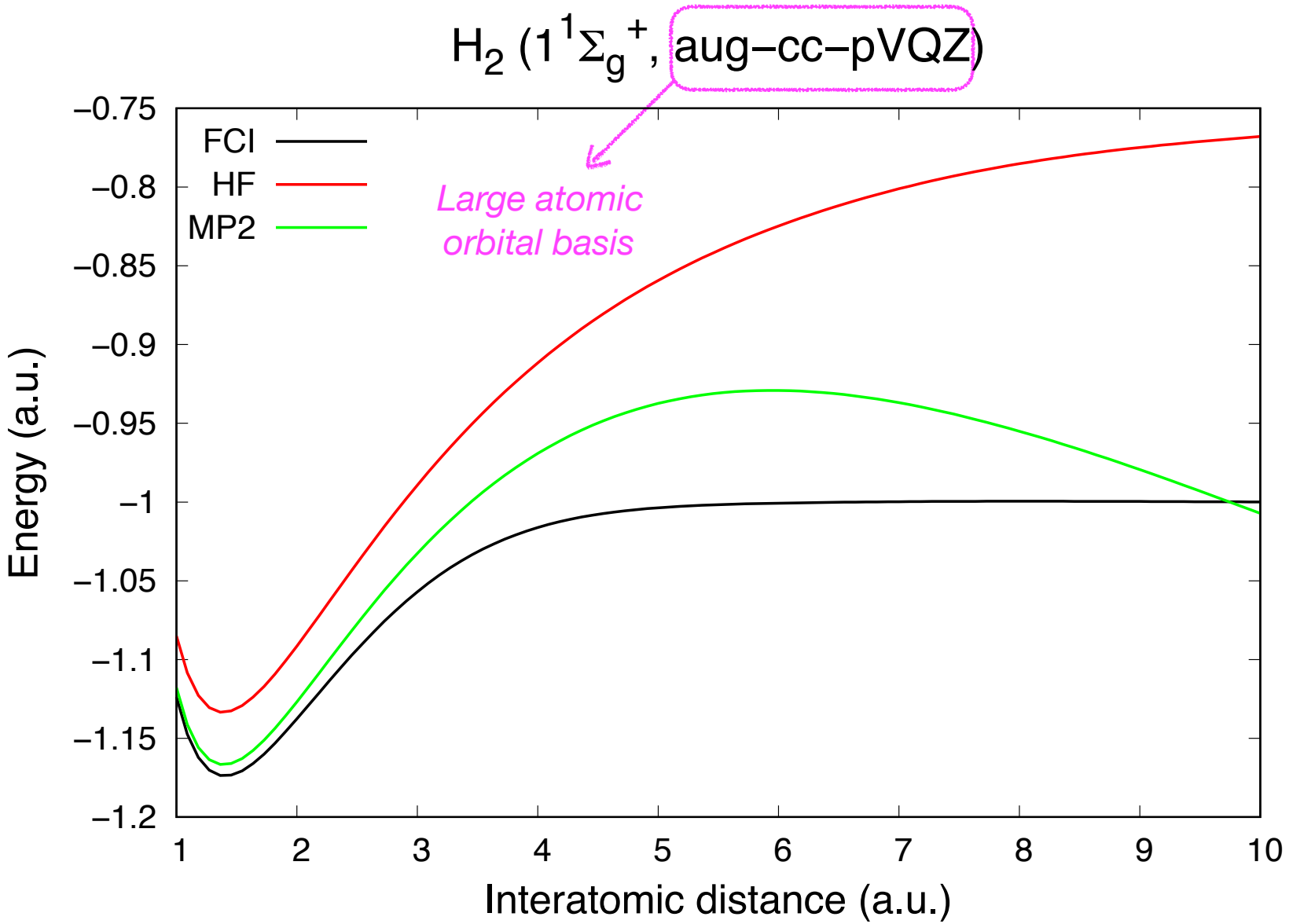
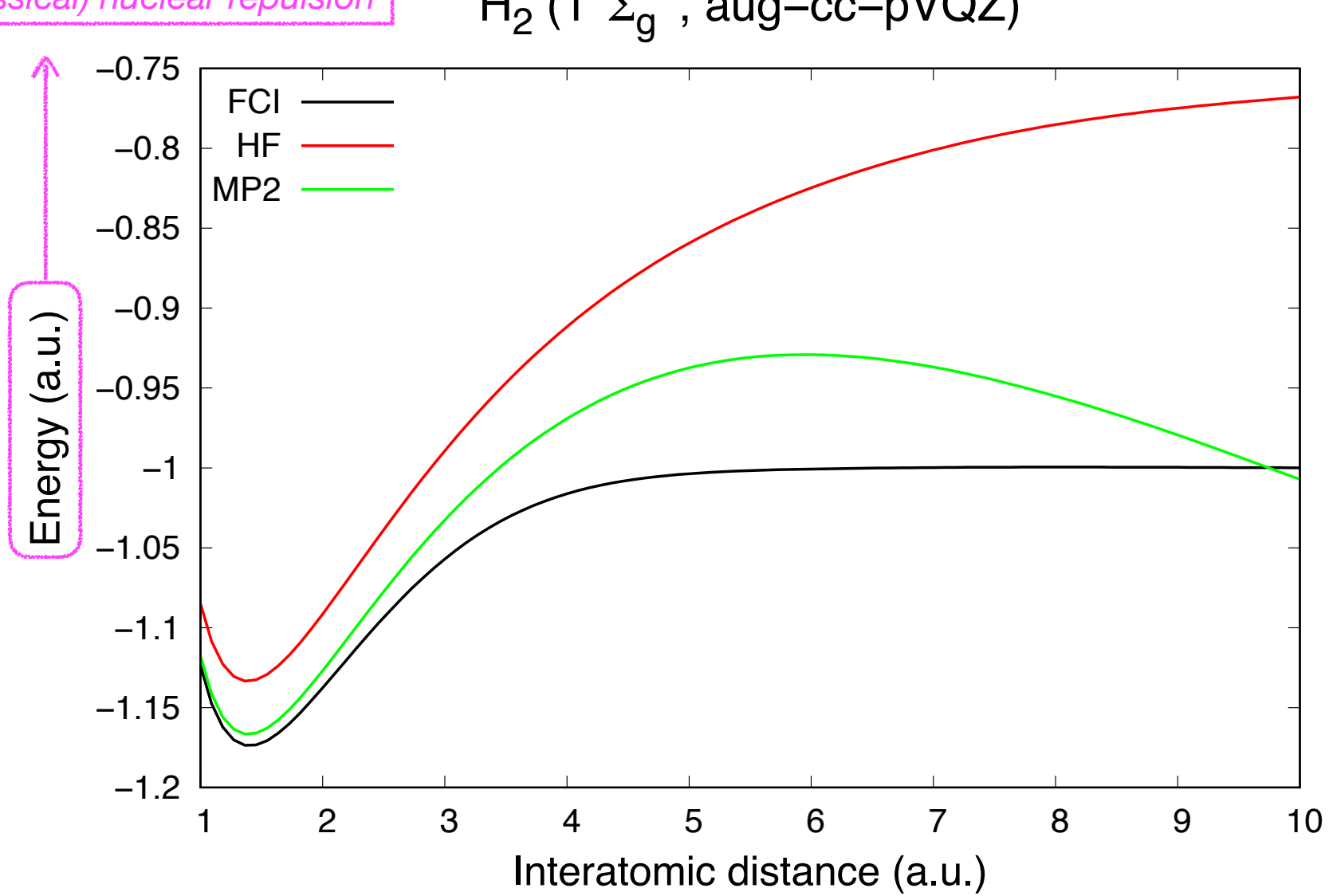
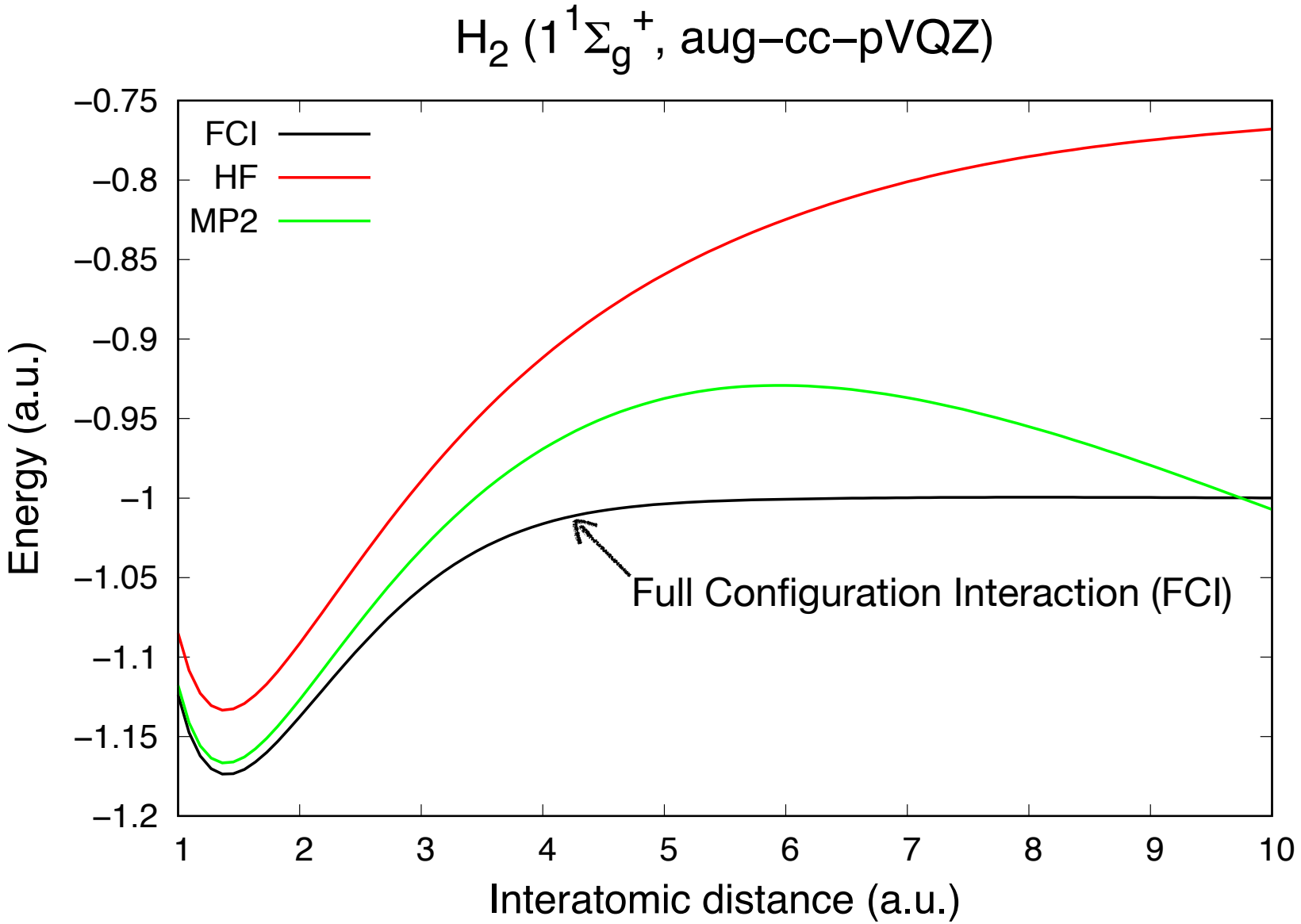


Dissociation of the hydrogen molecule

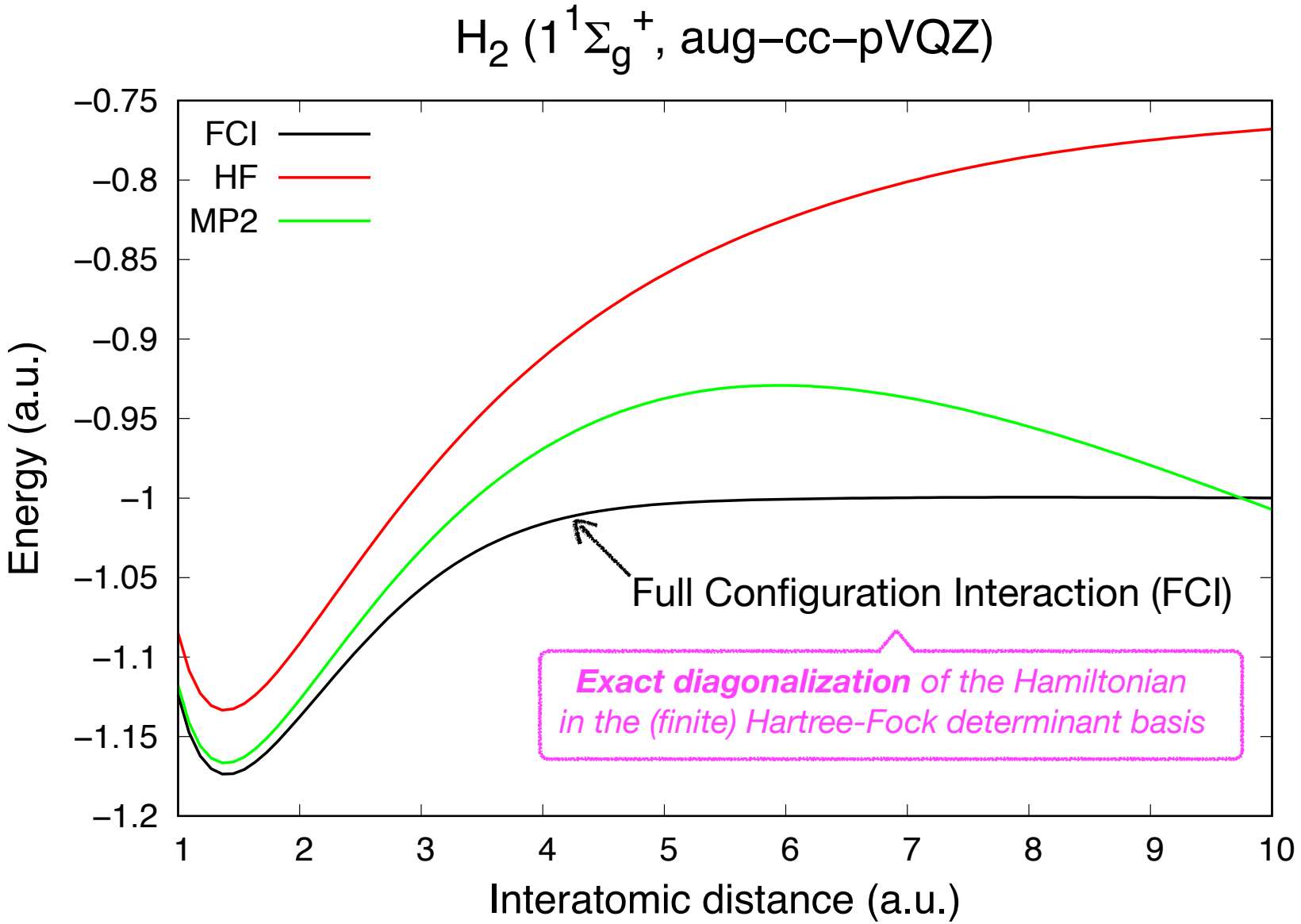
(Quantum) electronic energy
+
(classical) nuclear repulsion



Dissociation of the hydrogen molecule



Dissociation of the hydrogen molecule



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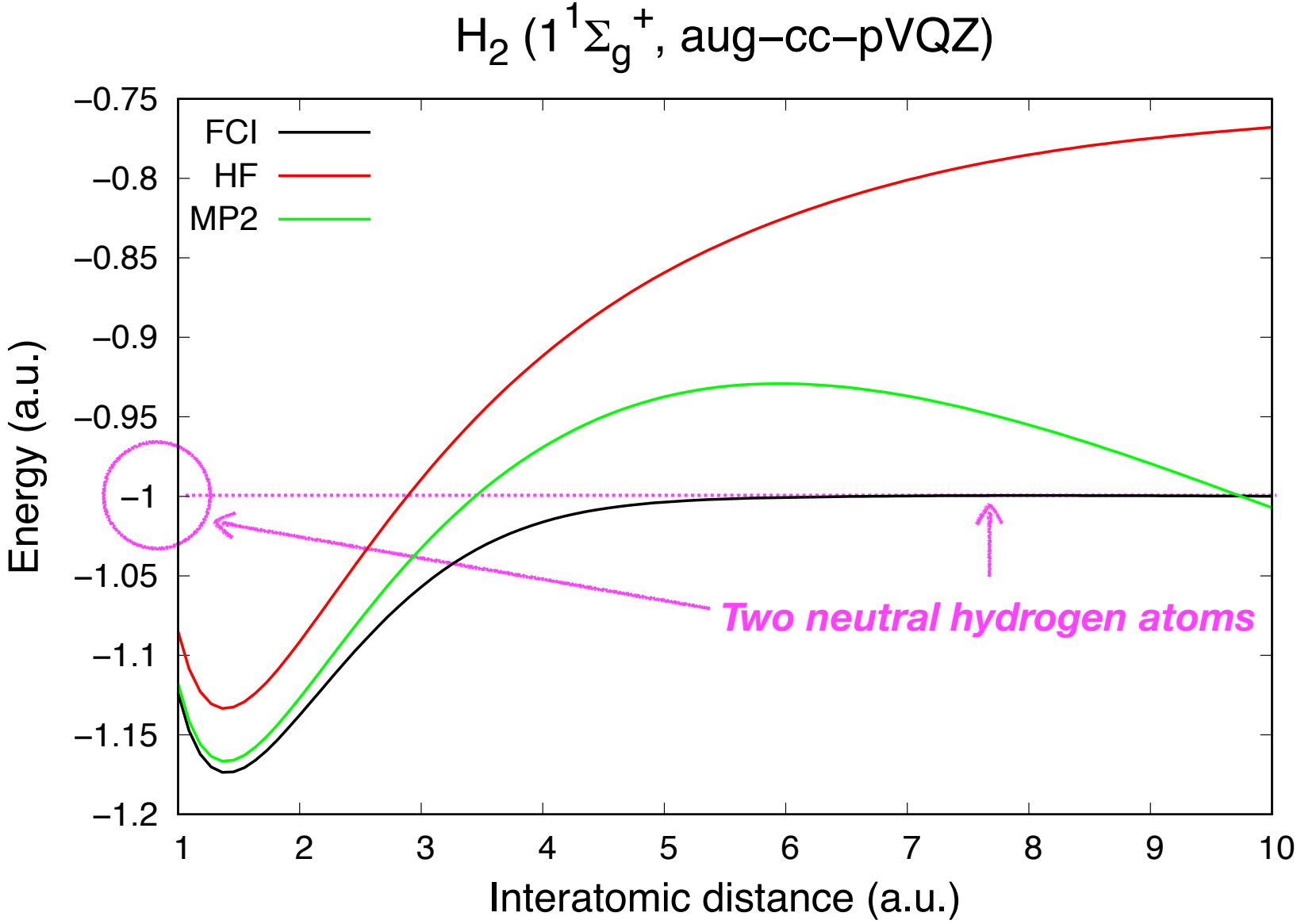

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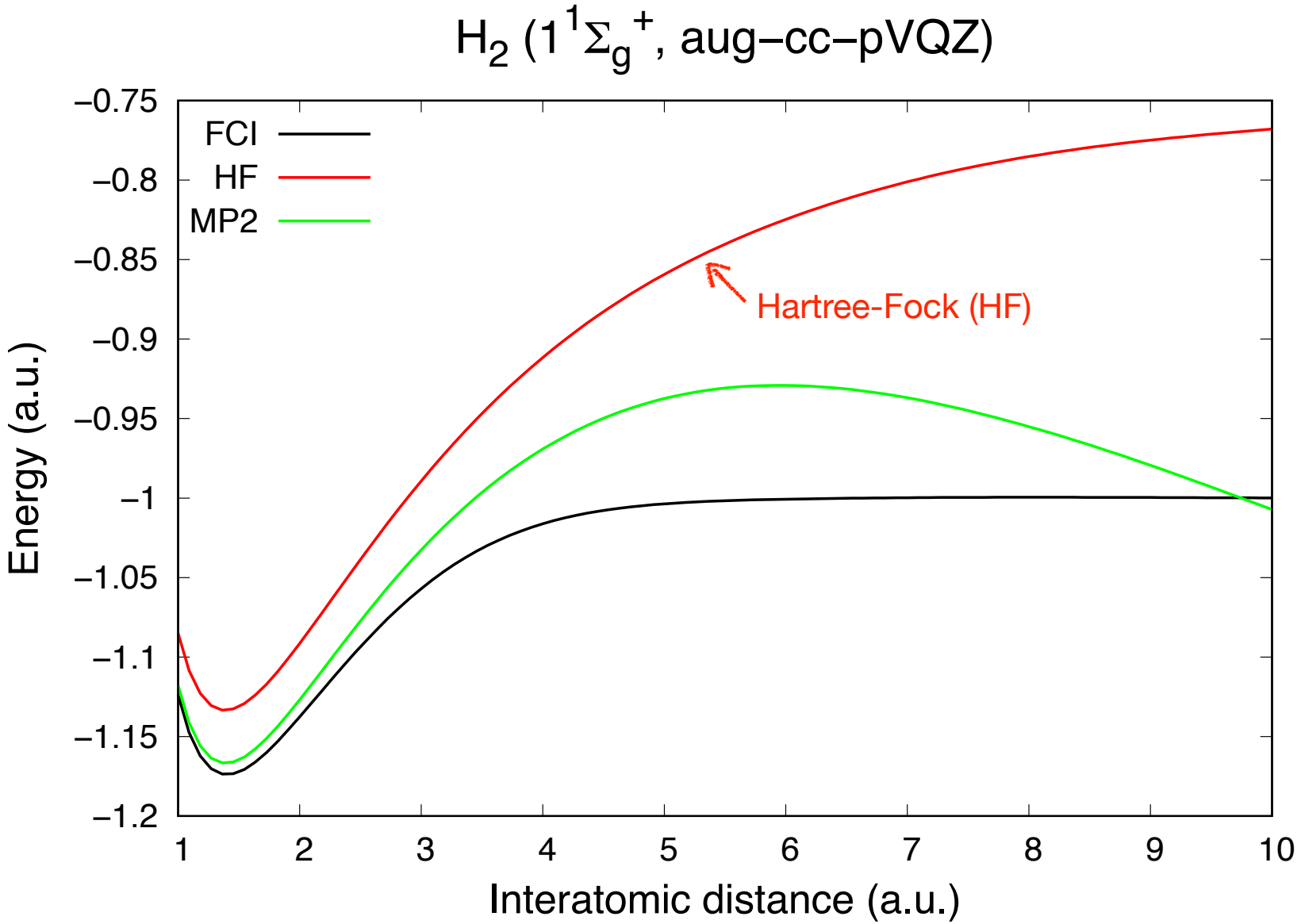

Dissociation of the hydrogen molecule

Restricted Hartree-Fock (HF)

$$|\Psi\rangle \approx \left| \left(1\sigma_g\right)^2 \right\rangle \equiv \hat{a}^{\dagger}_{1\sigma_g,\alpha} \hat{a}^{\dagger}_{1\sigma_g,\beta} |\,\mathrm{vac}\rangle$$

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$$\equiv \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

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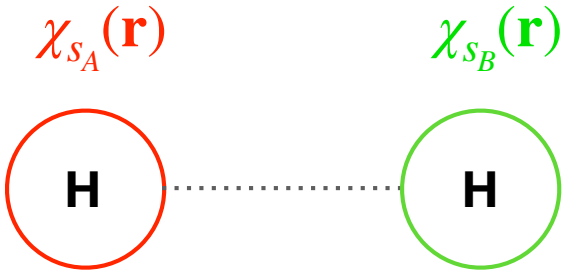
$$\equiv \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

Bonding orbital

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$



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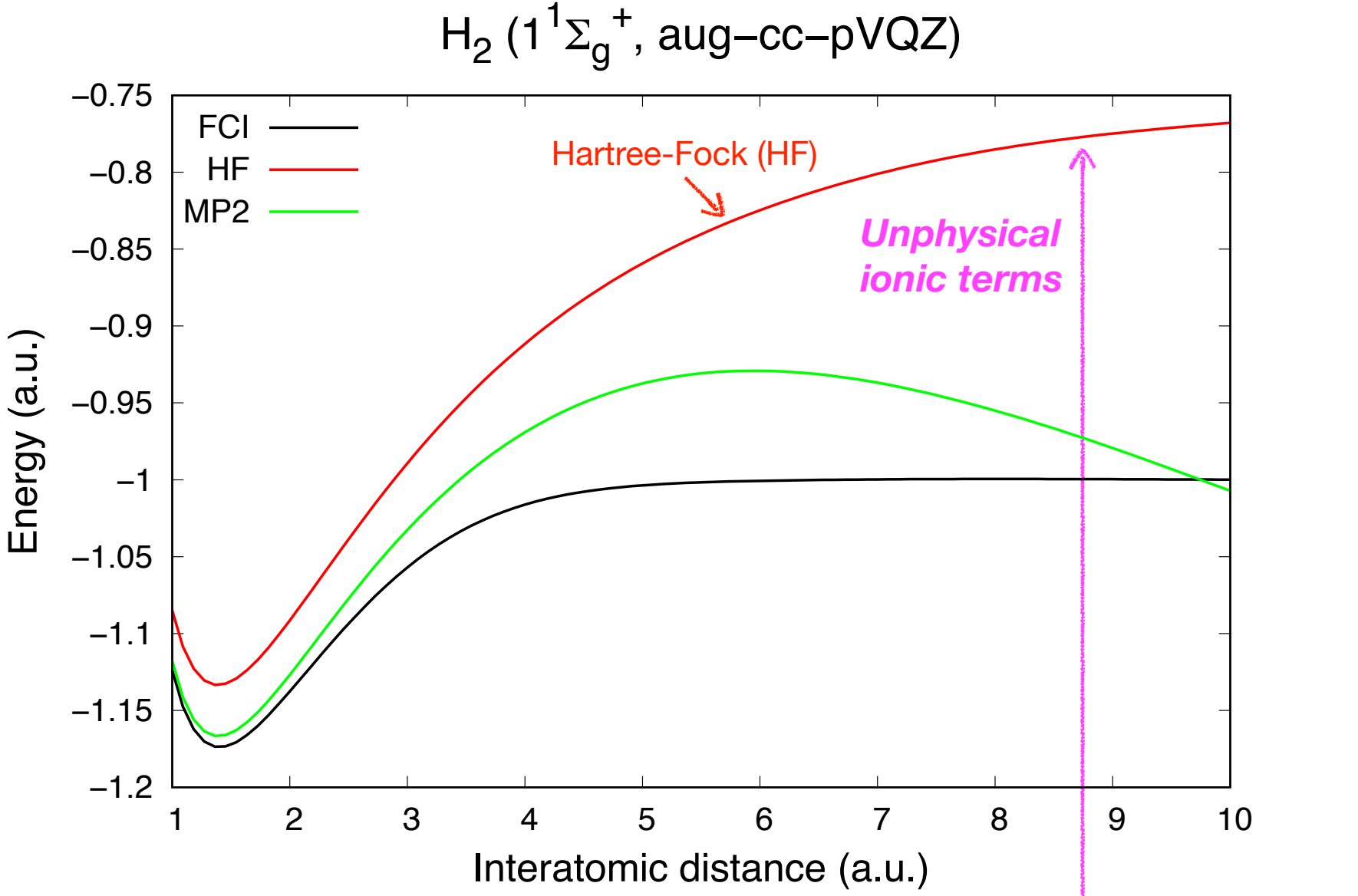
$$\equiv \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

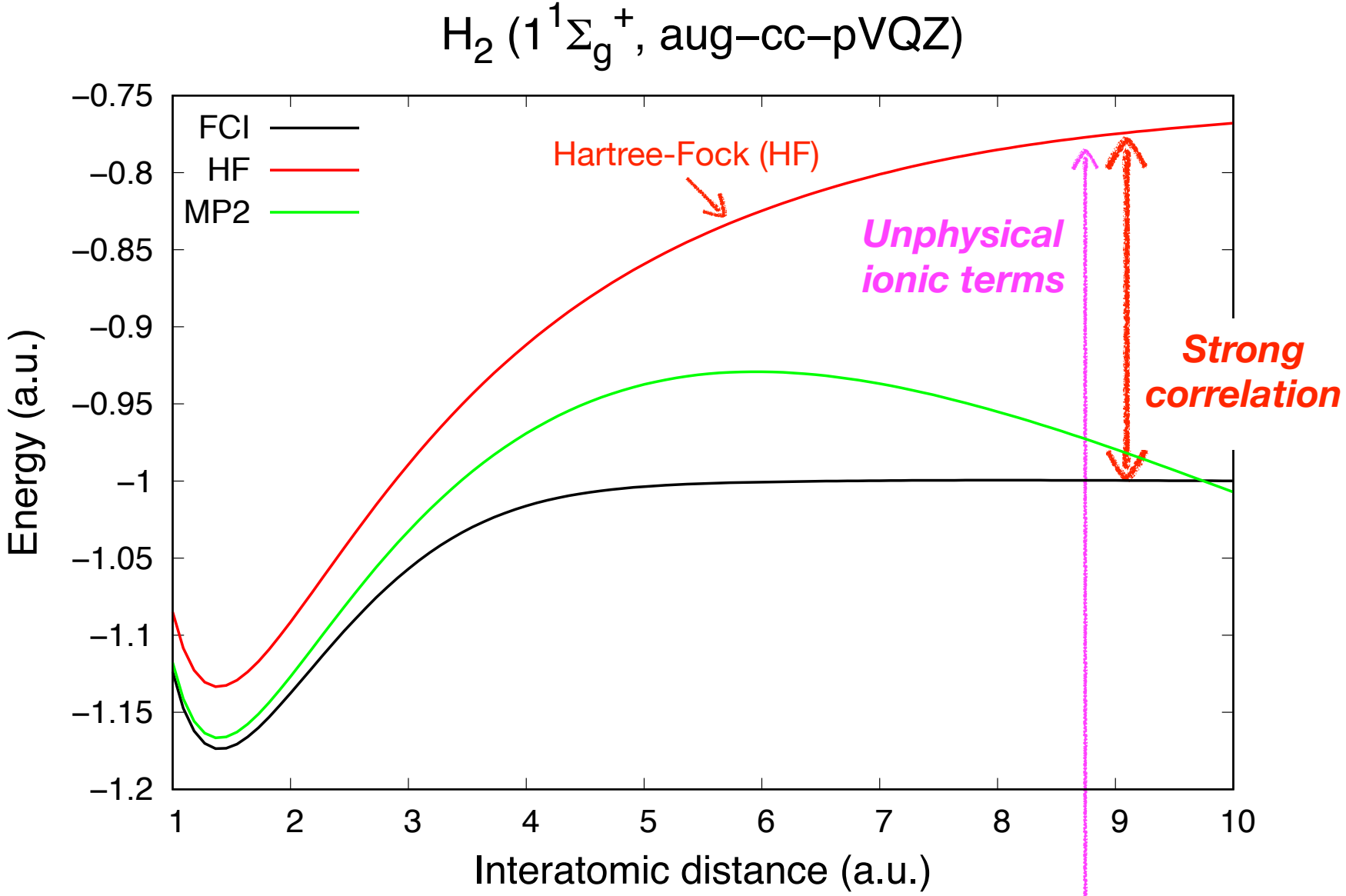
$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

H ..... H H ..... H

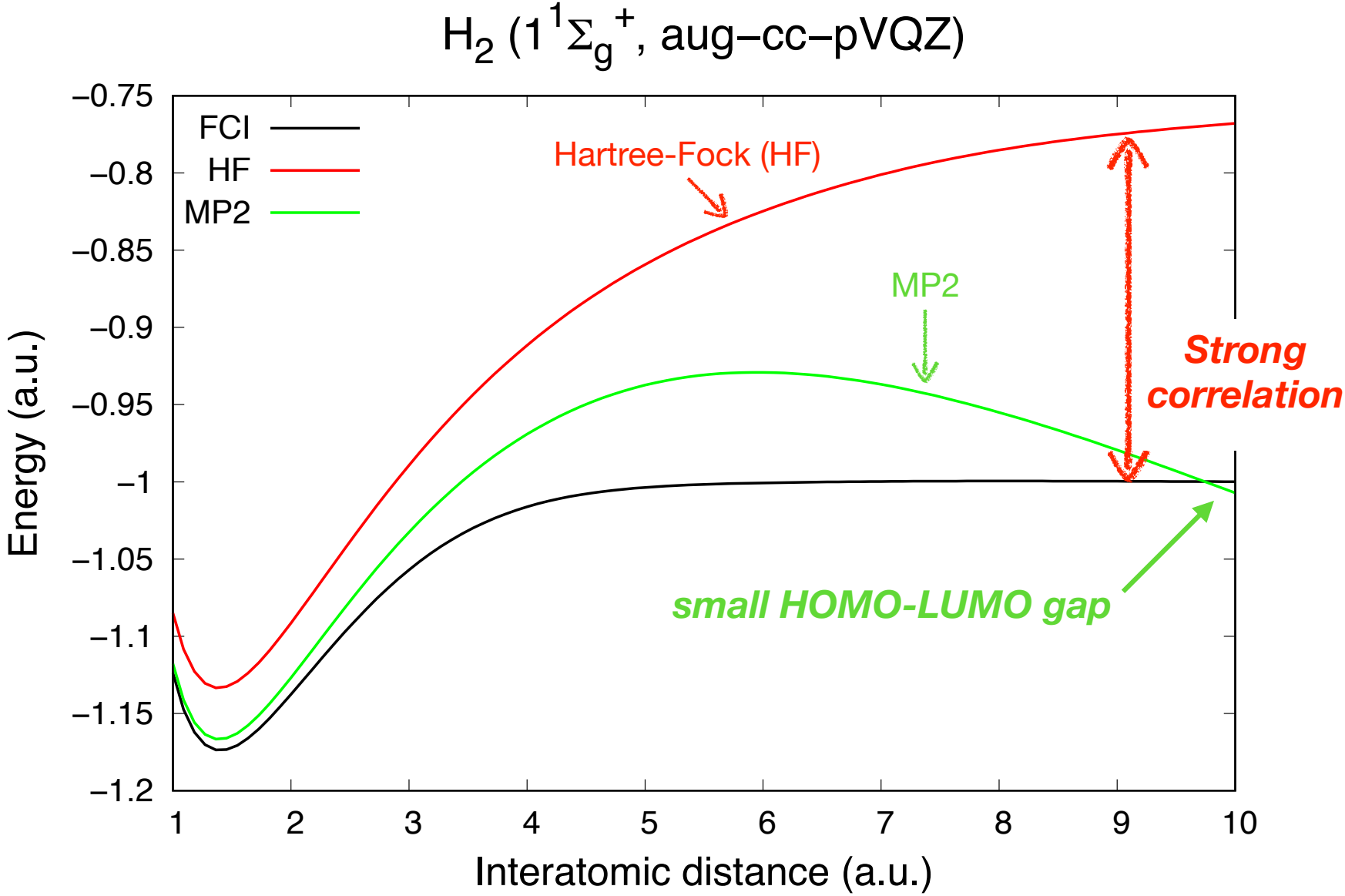


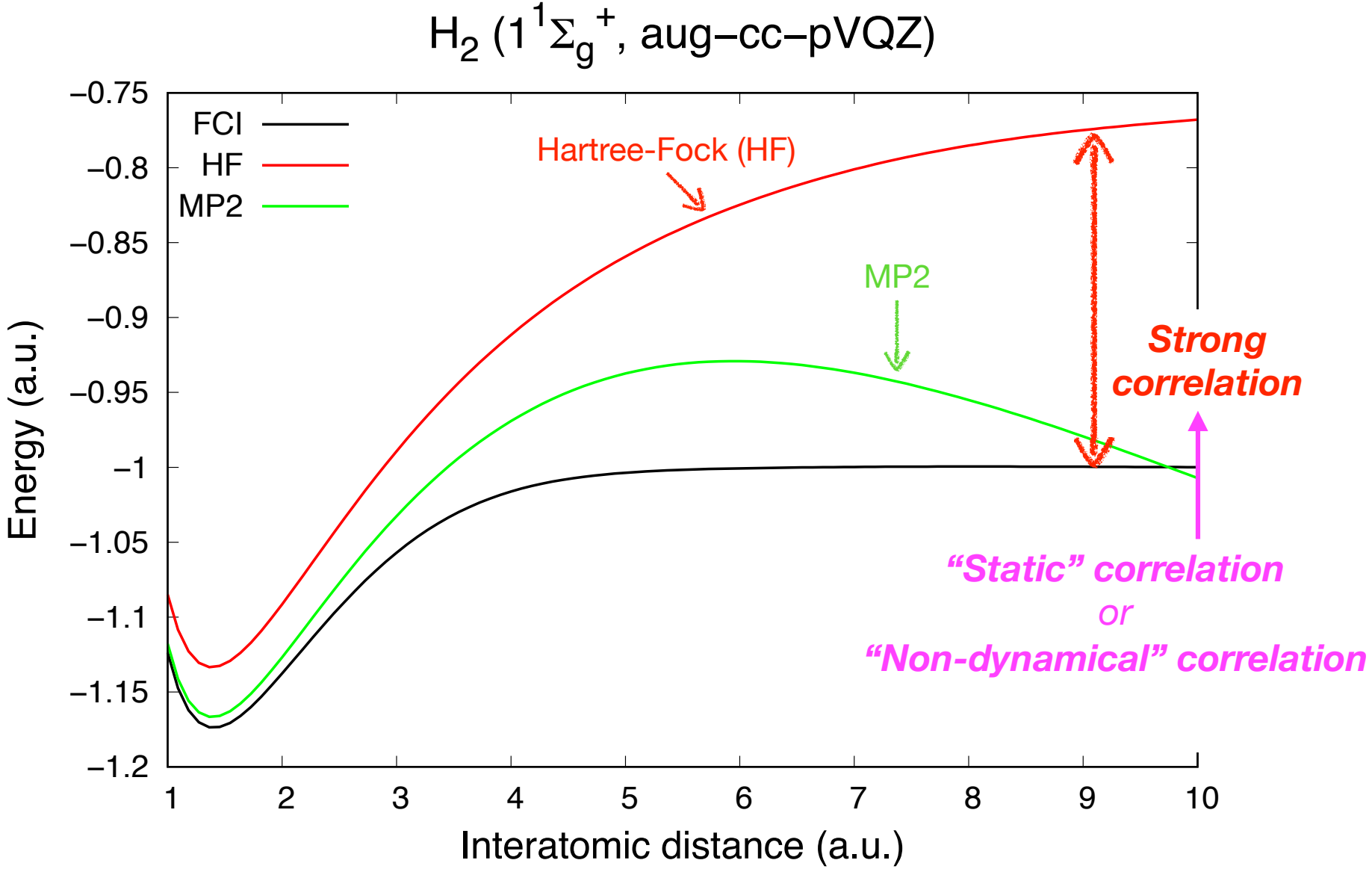
$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

$H^-\cdots H^+$ $H^+\cdots H^-$



$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$


H_2 ($1^1\Sigma_g^+$, aug–cc–pVQZ)
FCI
HF
MP2
Hartree-Fock (HF)
MP2
Strong correlation
small HOMO-LUMO gap
Energy (a.u.)
Interatomic distance (a.u.)
–0.75
–0.8
–0.85
–0.9
–0.95
–1
–1.05
–1.1
–1.15
–1.2
1
2
3
4
5
6
7
8
9
10


H_2 ($1^1\Sigma_g^+$, aug–cc–pVQZ)
FCI
HF
MP2
Hartree-Fock (HF)
MP2
Strong correlation
"Static" correlation
or
"Non-dynamical" correlation
Energy (a.u.)
Interatomic distance (a.u.)
–0.75
–0.8
–0.85
–0.9
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–1
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1
2
3
4
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7
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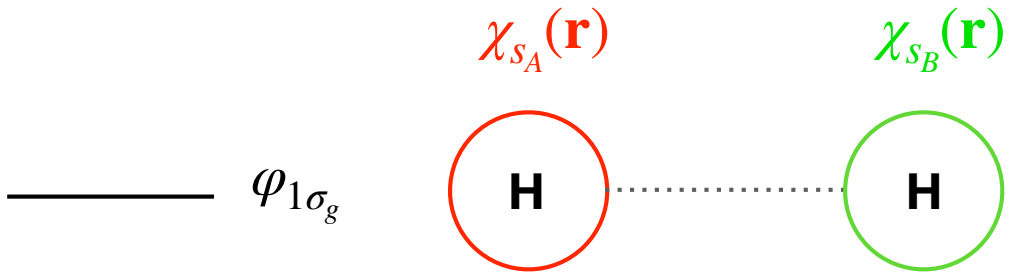
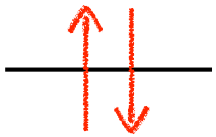
10

Multi-configurational wave function



Multi-configurational wave function

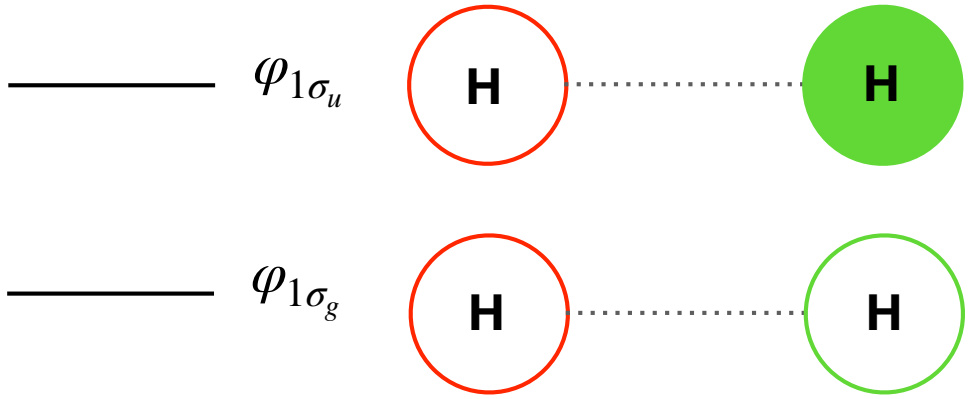


$\varphi_{1\sigma_g}$

$$\left| \left(1\sigma_g\right)^2 \right\rangle$$

Hartree-Fock: ***single configuration*** method

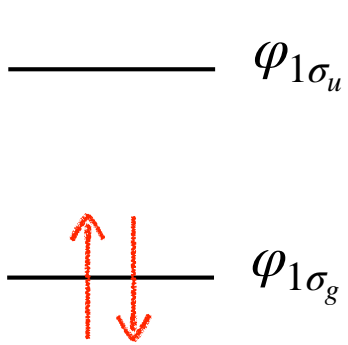
Multi-configurational wave function

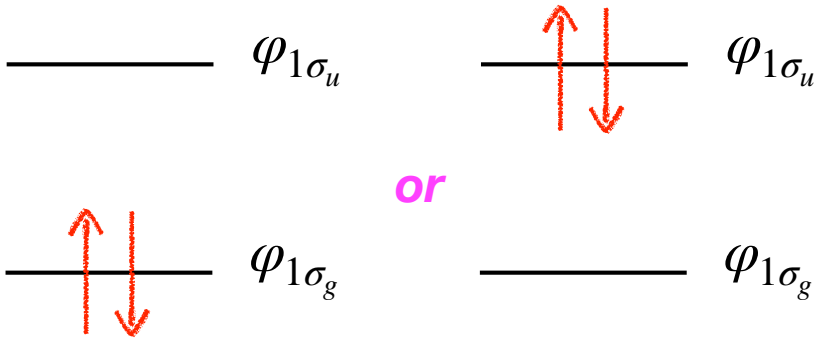


$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

Anti-bonding orbital

Multi-configurational wave function

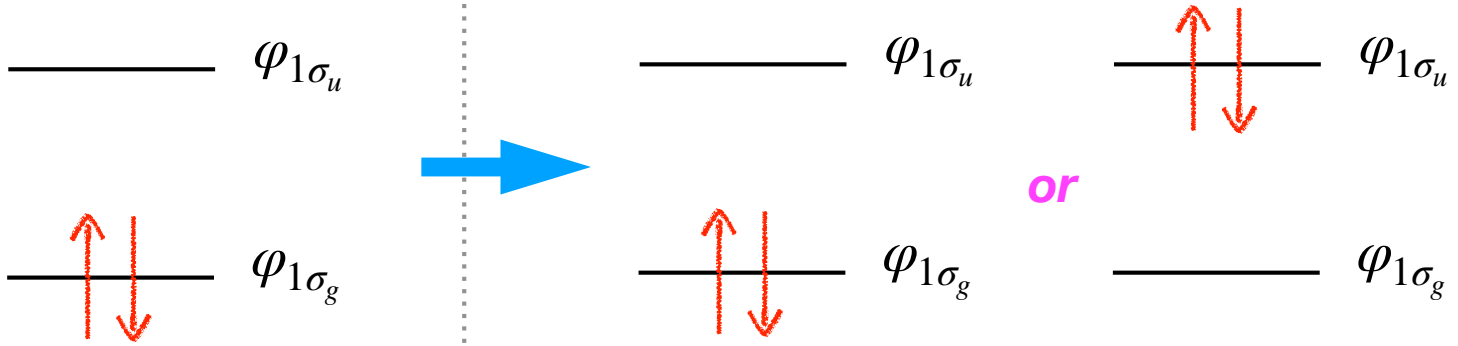




$$\left|\left(1\sigma_g\right)^2\right\rangle$$

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left[\left|\left(1\sigma_g\right)^2\right\rangle - \left|\left(1\sigma_u\right)^2\right\rangle\right]$$

Multi-configurational wave function



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$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Multi-configurational wave function

$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

$$\Psi \equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

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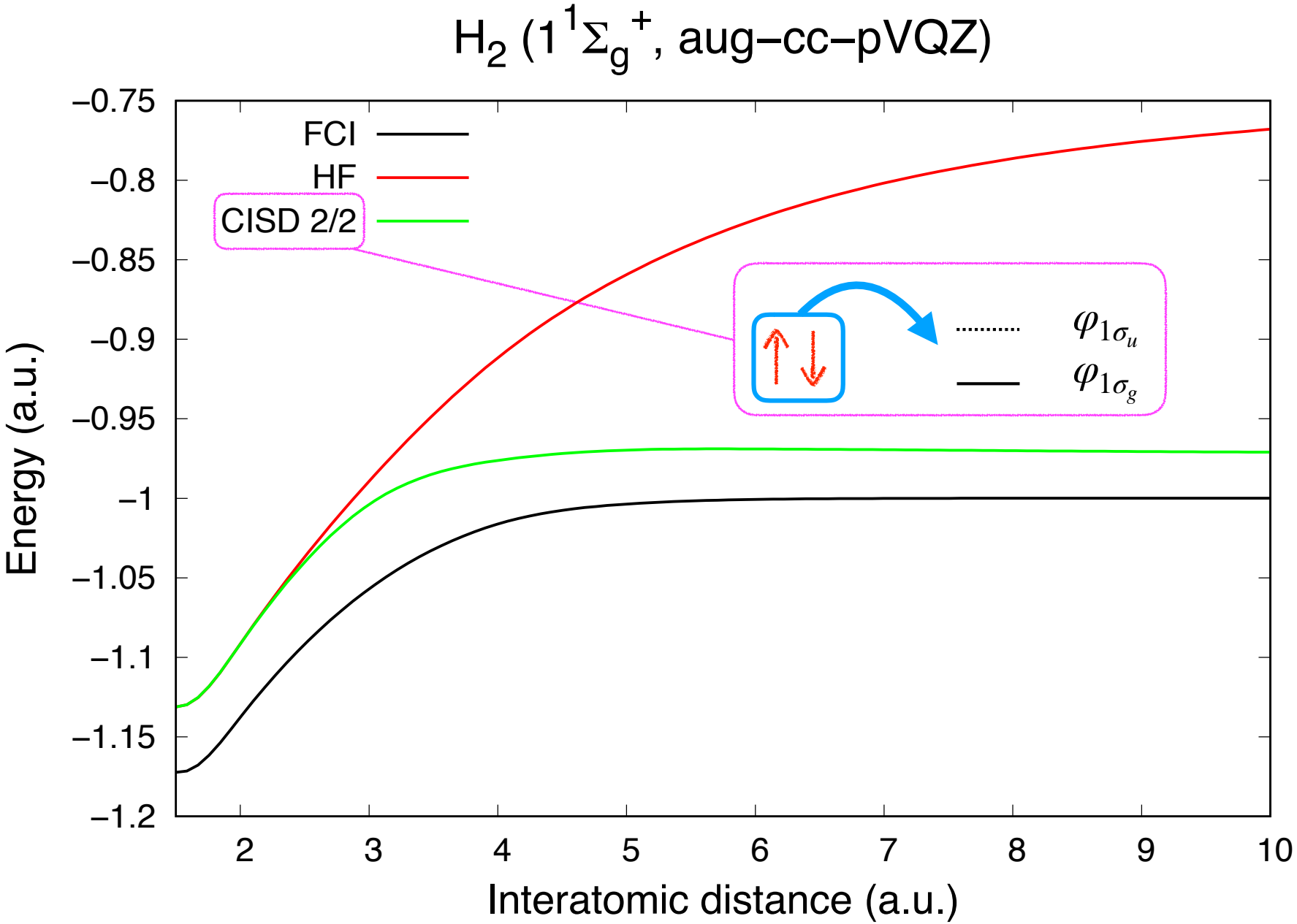
$$\Psi \equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

H ..... H H ..... H

Dissociation of the hydrogen molecule



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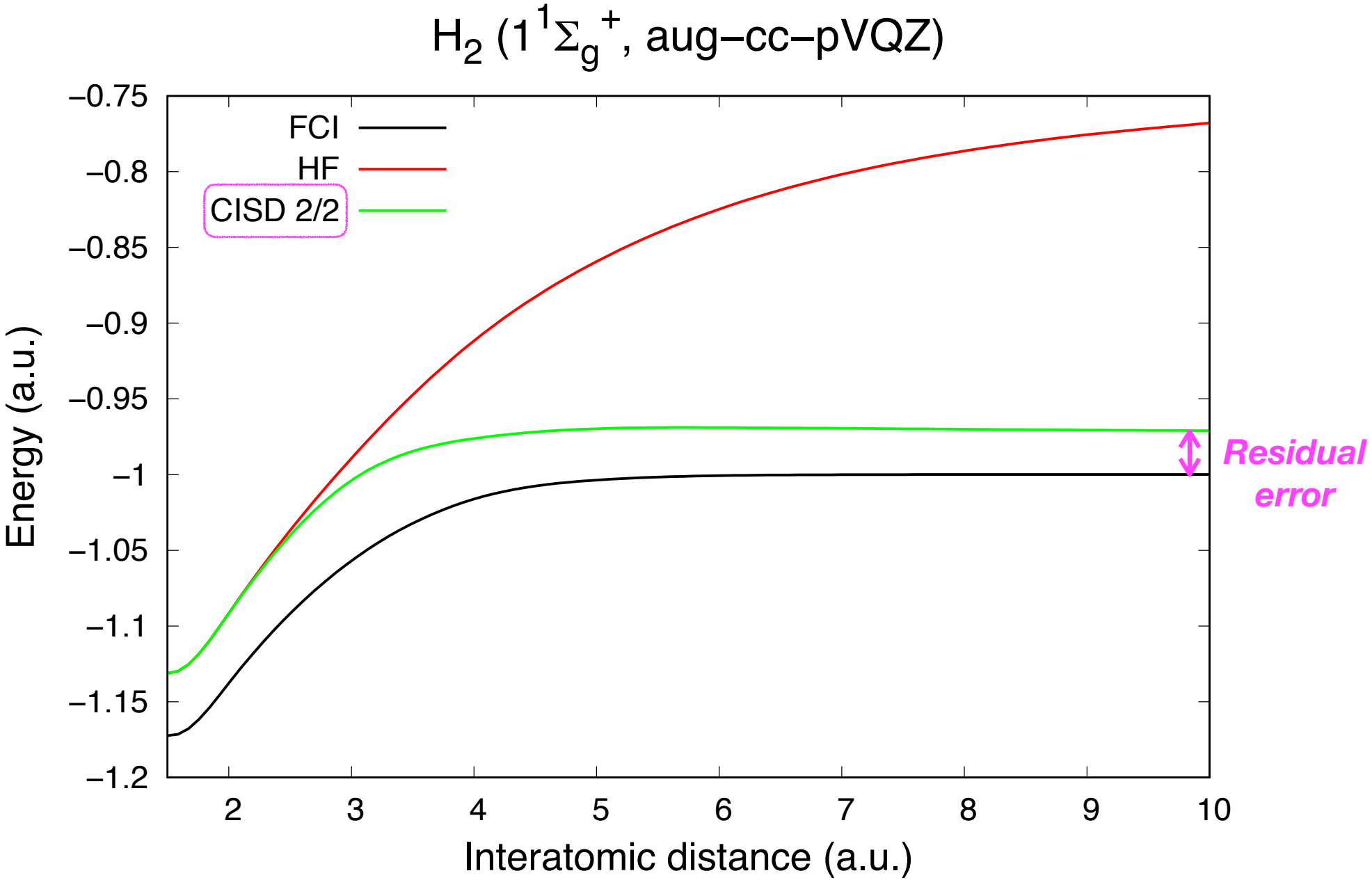

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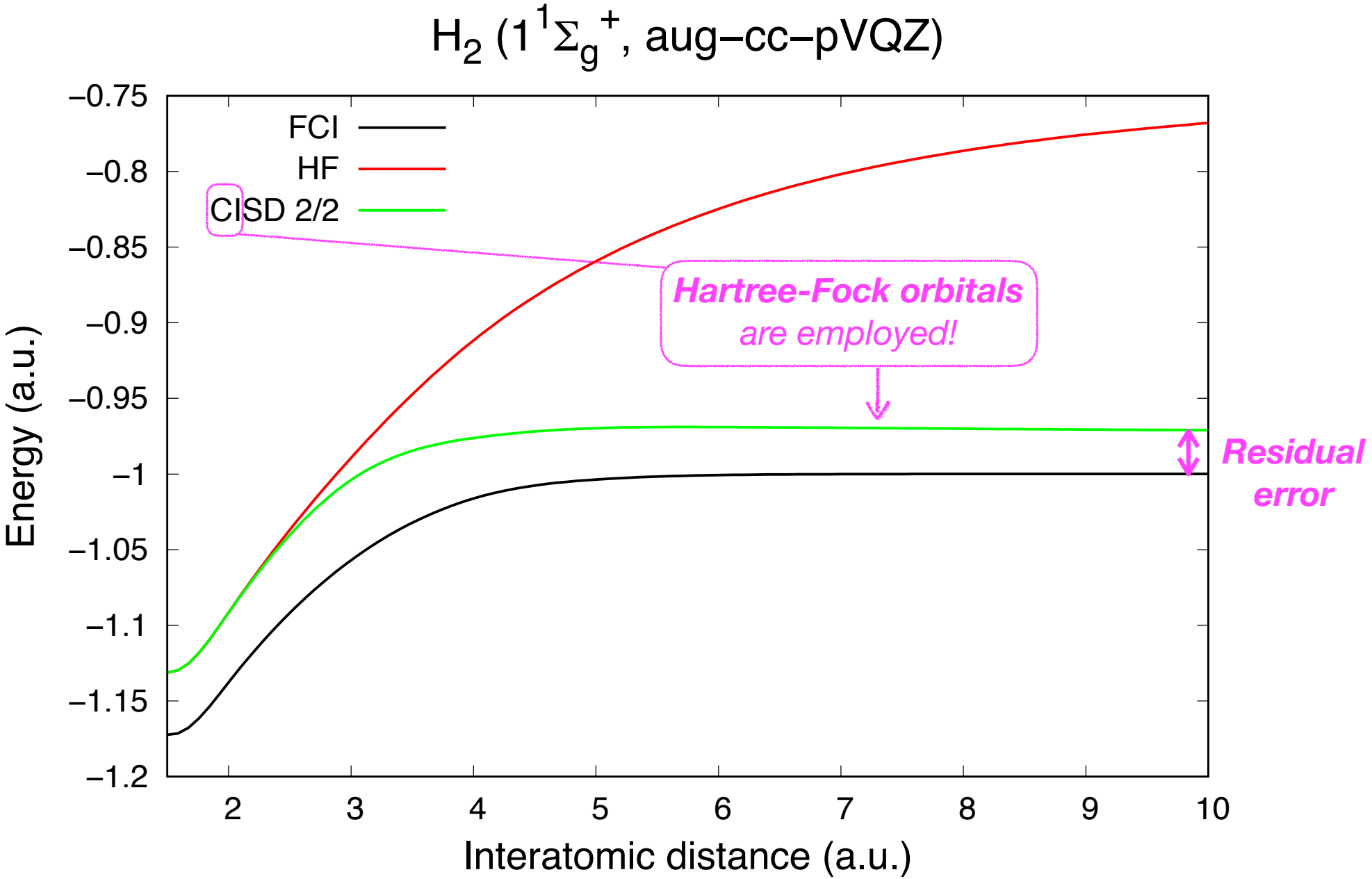

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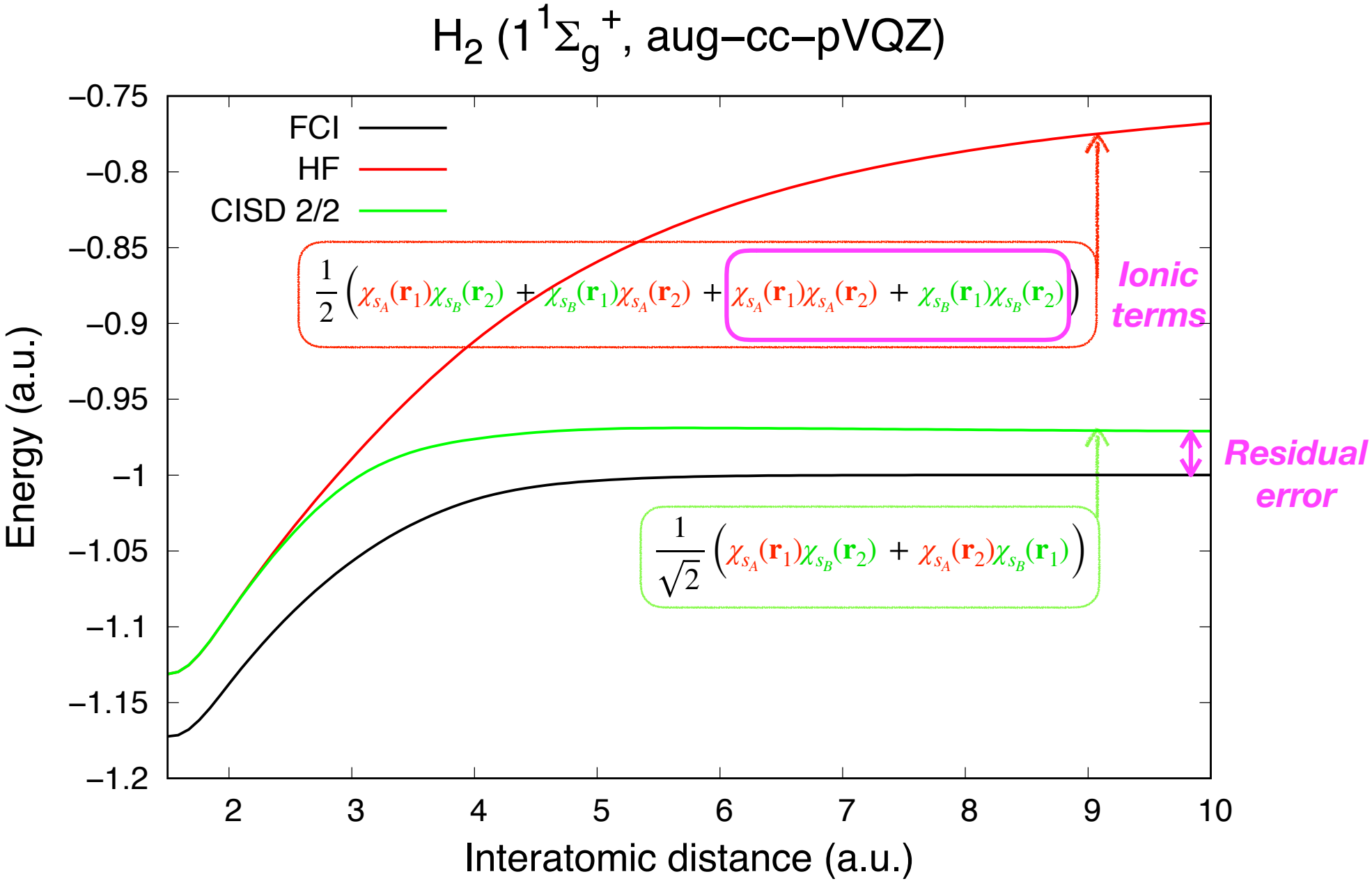

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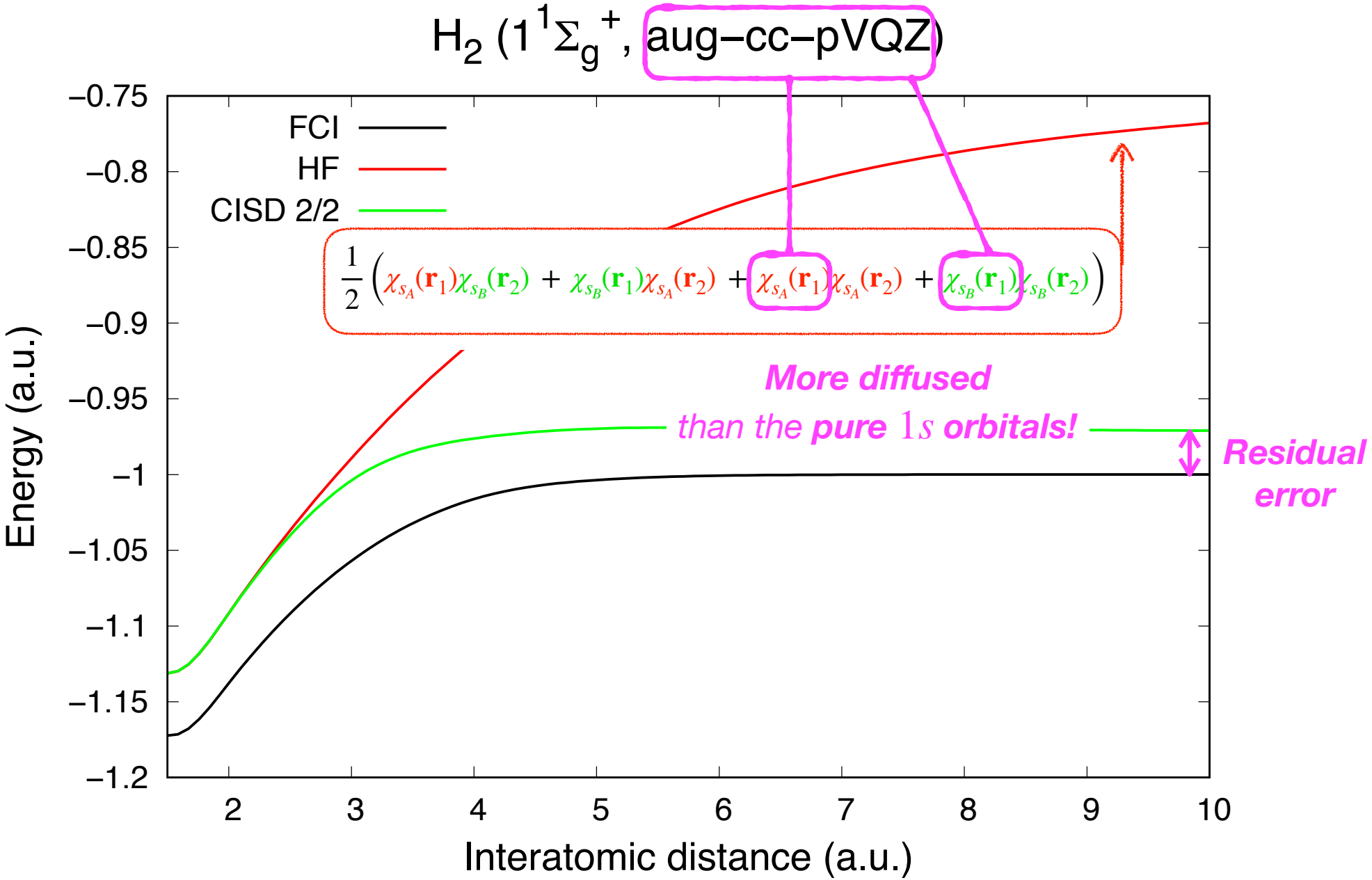

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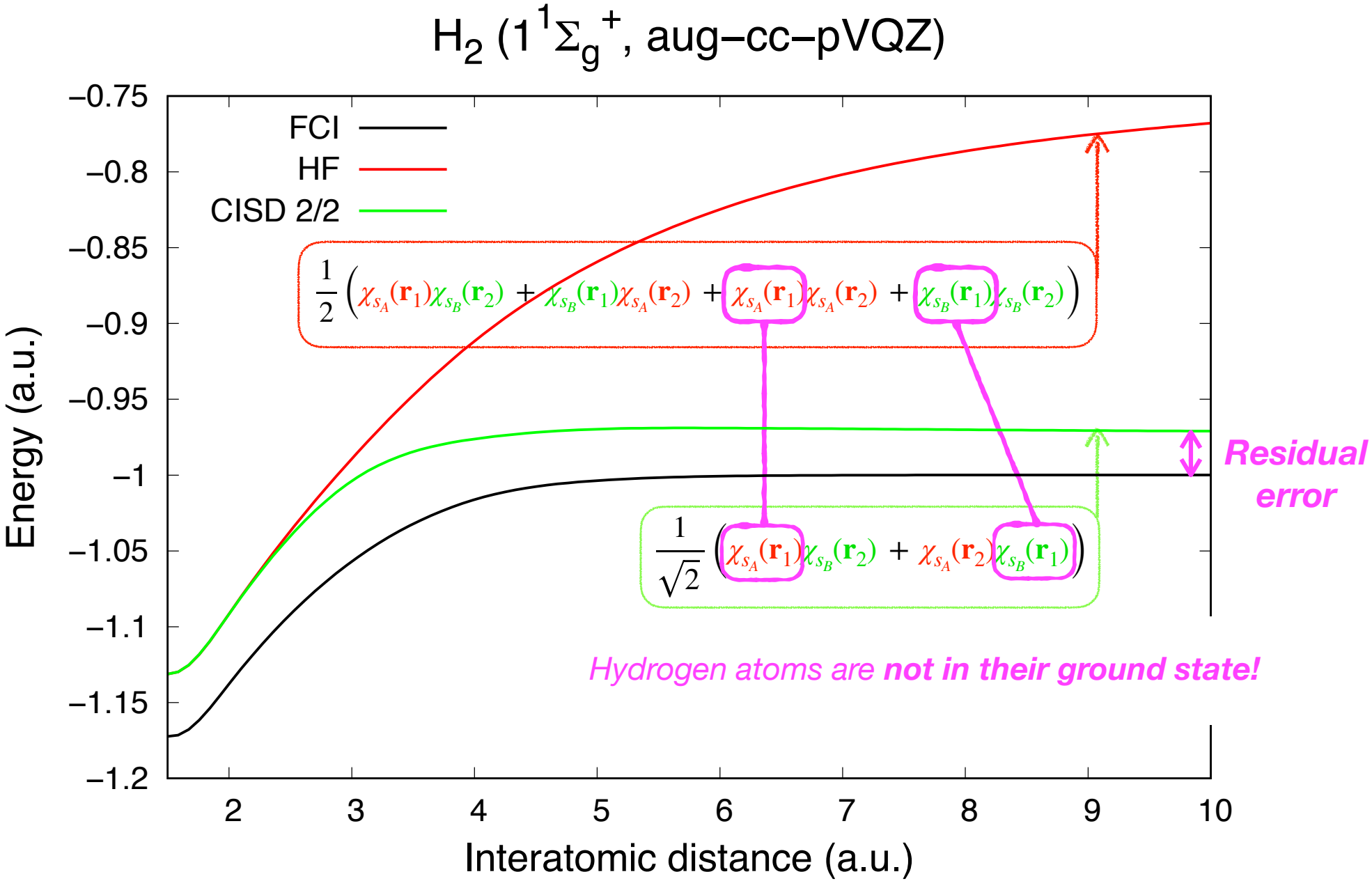

What did we learn?

Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Outline

- Strong electron correlation regime

The prototypical hydrogen molecule at dissociation

- Orbital rotation in second quantization

Orbital optimisation procedure

- **C**omplete **A**ctive **S**pace **S**elf-**C**onsistent **F**ield and beyond

General CASSCF approach, state-averaging,
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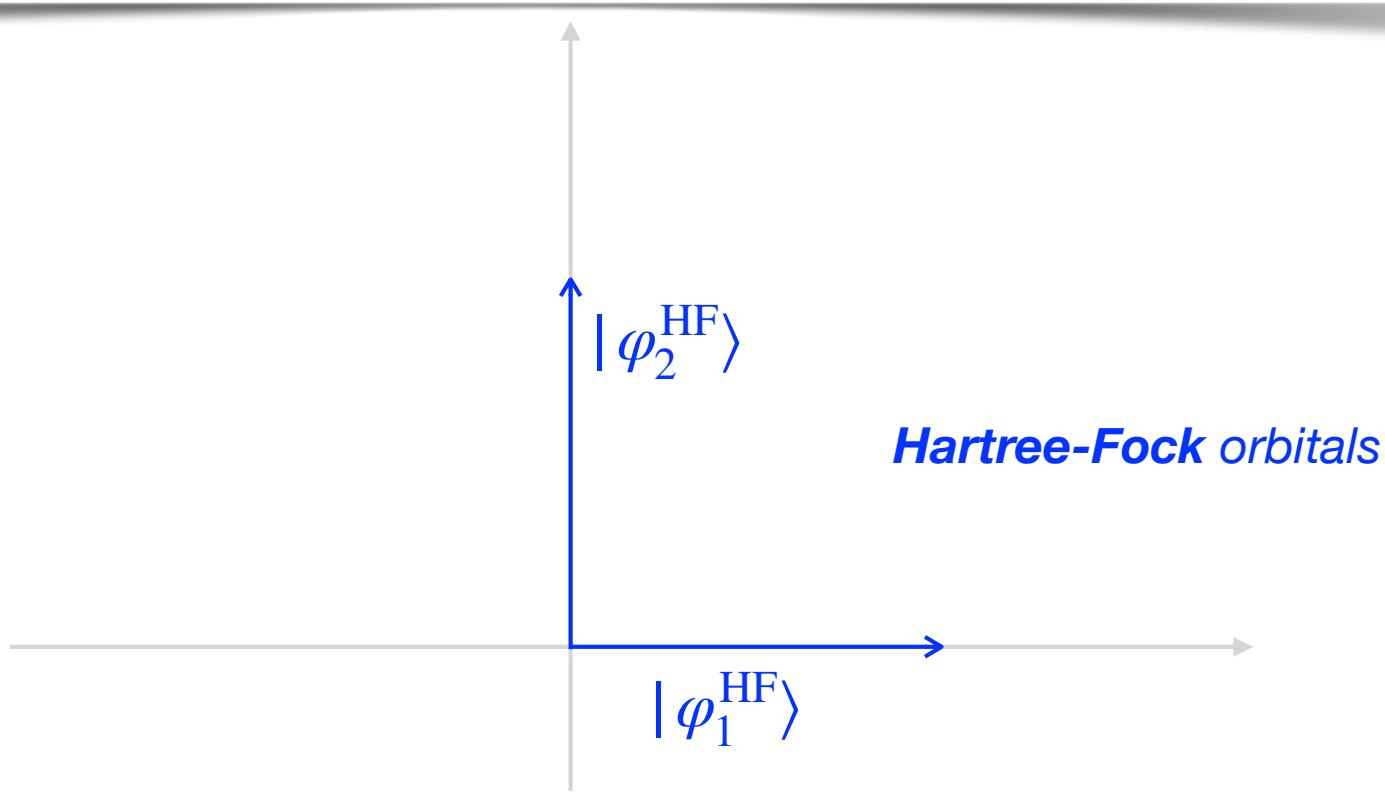
What did we learn?

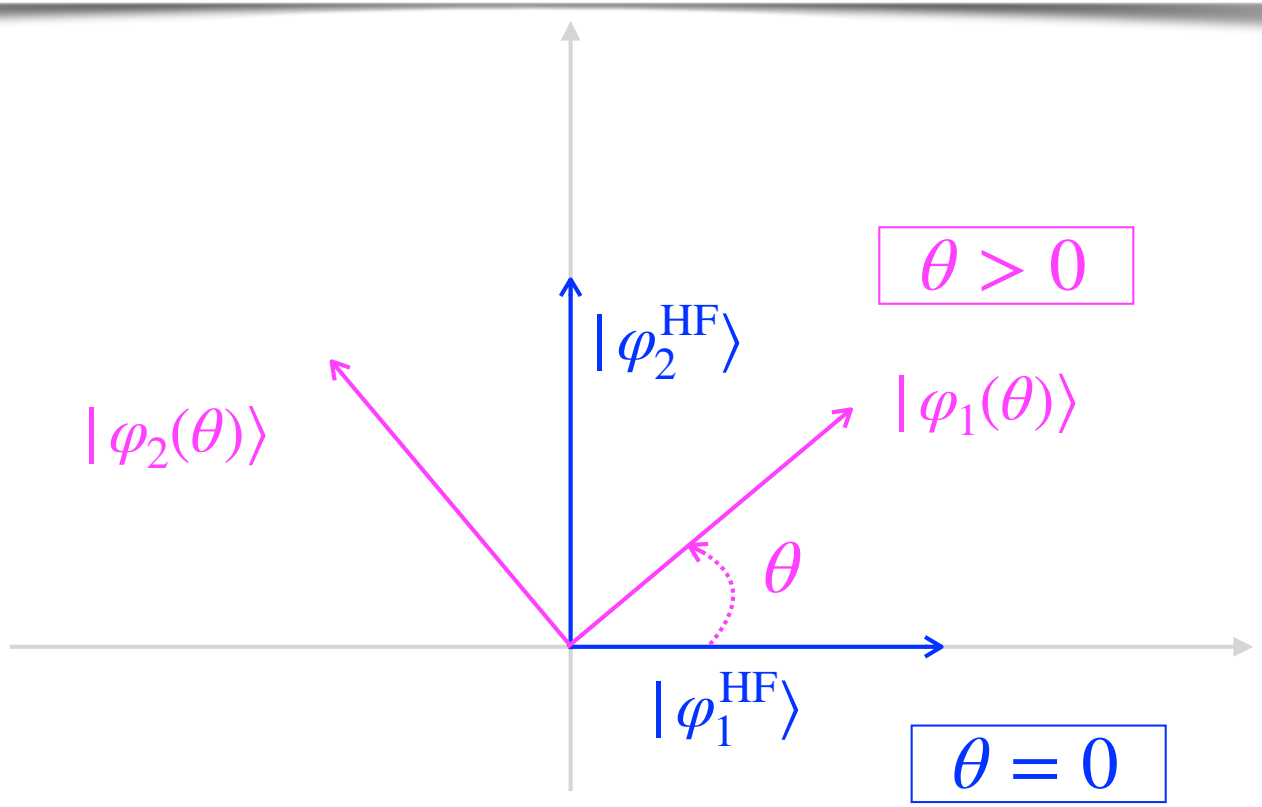
Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Multi-Configurational Self-Consistent Field (MCSCF) approach

Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

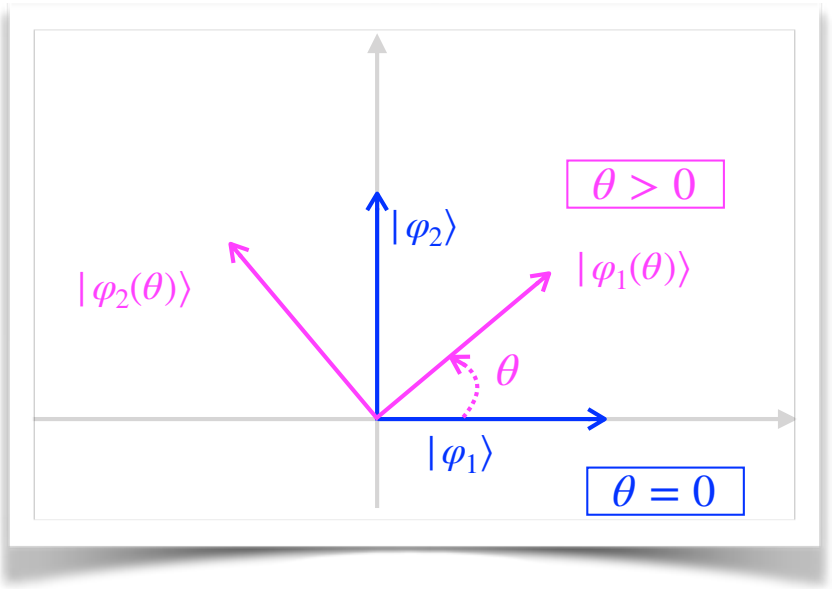


Multi-configurational *wave functions need a* ***re-optimization*** ***of the orbitals***



Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

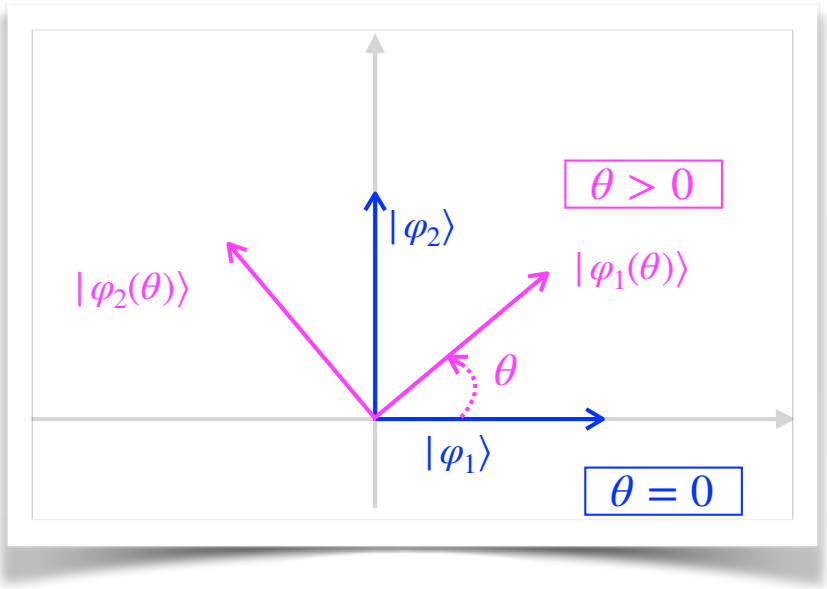


Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

$$\begin{array}{c} \\ \langle\varphi_1| \\ \langle\varphi_2| \end{array} \begin{array}{c} \begin{array}{cc} |\varphi_1(\theta)\rangle & |\varphi_2(\theta)\rangle \end{array} \\ \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \end{array}$$

Matrix representation of the rotation



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Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

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Angle matrix

$$\underline{\underline{\theta}}$$

Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

$$\begin{array}{c} \\ \langle\varphi_1| \\ \langle\varphi_2| \end{array} \begin{array}{c} \begin{array}{cc} |\varphi_1(\theta)\rangle & |\varphi_2(\theta)\rangle \end{array} \\ \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \end{array} = e^{-\begin{bmatrix} 0 & \theta \\ -\theta & 0 \end{bmatrix}}$$

$$\underline{\underline{\theta}} = -\underline{\underline{\theta}}^{\dagger}$$ ***anti-hermitian!***

Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

$$\begin{array}{c} \\ \langle\varphi_1| \\ \langle\varphi_2| \end{array} \begin{array}{c} \begin{array}{cc} |\varphi_1(\theta)\rangle & |\varphi_2(\theta)\rangle \end{array} \\ \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \end{array} = e^{-\underline{\underline{\theta}}}$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \ldots$$

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

After rotation

Before rotation

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Rotation operator

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}}|\varphi_P\rangle$$

$$\begin{bmatrix} 0 & \theta \\ -\theta & 0 \end{bmatrix} = \underline{\underline{\theta}} \longrightarrow \hat{\theta} \equiv \sum_{P,Q} \theta_{PQ} \hat{a}_P^\dagger \hat{a}_Q$$

One-electron
"angle"operator

$$= \theta\left(\hat{a}_1^\dagger \hat{a}_2 - \hat{a}_2^\dagger \hat{a}_1\right)$$

See my lecture on second quantization

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Single operator that rotates any spin-orbital

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Single operator that rotates any spin-orbital

Applies also to **Slater determinants**

$$\hat{a}^\dagger_{P_1(\theta)}\hat{a}^\dagger_{P_2(\theta)}\ldots\hat{a}^\dagger_{P_{N-1}(\theta)}\hat{a}^\dagger_{P_N(\theta)}|\text{vac}\rangle = e^{-\hat{\theta}}\hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\text{vac}\rangle$$

Rotated determinant — *Unrotated determinant*

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Single operator that rotates any spin-orbital

Applies also to **Slater determinants**

Applies also to **multi-configurational wave functions**

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Applies also to **multi-configurational wave functions**

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

Initial CI wave function

Spin-orbital rotation operator in second quantization

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Applies also to **multi-configurational wave functions**

$$\sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N} \hat{a}^\dagger_{P_1(\theta)} \hat{a}^\dagger_{P_2(\theta)} \ldots \hat{a}^\dagger_{P_{N-1}(\theta)} \hat{a}^\dagger_{P_N(\theta)} |\text{vac}\rangle = |\Psi(\theta)\rangle$$

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Initial CI wave function

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

Spin-orbital rotation operator in second quantization

$$|\varphi_P(\theta)\rangle = e^{-\hat{\theta}} |\varphi_P\rangle$$

Applies also to **multi-configurational wave functions**

Initial CI wave function

$$e^{-\hat{\theta}} |\Psi\rangle = |\Psi(\theta)\rangle$$

Energy minimisation

$$E = \langle e^{-\hat{\theta}} \Psi \,|\, \hat{H} \,|\, e^{-\hat{\theta}} \Psi \rangle \equiv E(\theta)$$

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$$= \langle \Psi \,|\, (1+\hat{\theta}+\frac{1}{2}\hat{\theta}^2+\ldots)\, \hat{H}\, (1-\hat{\theta}+\frac{1}{2}\hat{\theta}^2-\ldots) \,|\, \Psi \rangle$$

Energy minimisation

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$$\approx E(0) + \theta E^{[1]} + \frac{\theta^2}{2} E^{[2]}$$

Gradient

Hessian

*Taylor expansion through **second order***

Energy minimisation

$$E = \langle e^{-\hat{\theta}}\Psi \,|\, \hat{H} \,|\, e^{-\hat{\theta}}\Psi \rangle \equiv E(\theta)$$

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$$\approx E(0) + \theta E^{[1]} + \frac{\theta^2}{2} E^{[2]}$$

Gradient

$$\hat{\theta} = \theta \left(\hat{a}_1^\dagger \hat{a}_2 - \hat{a}_2^\dagger \hat{a}_1 \right)$$

$$2 \left(\langle \hat{a}_2^\dagger \hat{a}_1 \Psi \,|\, \hat{H}\Psi \rangle - \langle \hat{a}_1^\dagger \hat{a}_2 \Psi \,|\, \hat{H}\Psi \rangle \right)$$

Energy ***couplings*** *with* ***singly excited*** *states*

Energy minimisation

$$E(\theta) \approx E(0) + \theta E^{[1]} + \frac{\theta^2}{2} E^{[2]}$$

$$\frac{dE(\theta)}{d\theta} = 0$$

$$\theta \approx -\frac{1}{E^{[2]}} E^{[1]}$$

Newton **step**

Energy minimisation

$$E(\theta) \approx E(0) + \theta E^{[1]} + \frac{\theta^2}{2} E^{[2]}$$

$$\frac{dE(\theta)}{d\theta} = 0$$

$$\theta \approx -\frac{1}{E^{[2]}} E^{[1]}$$

Iterative procedure!

Newton **step**

Energy minimisation

$$E(\theta) \approx E(0) + \theta E^{[1]} + \frac{\theta^2}{2} E^{[2]}$$

$$\frac{dE(\theta)}{d\theta} = 0$$

At convergence $\theta = 0 = E^{[1]}$

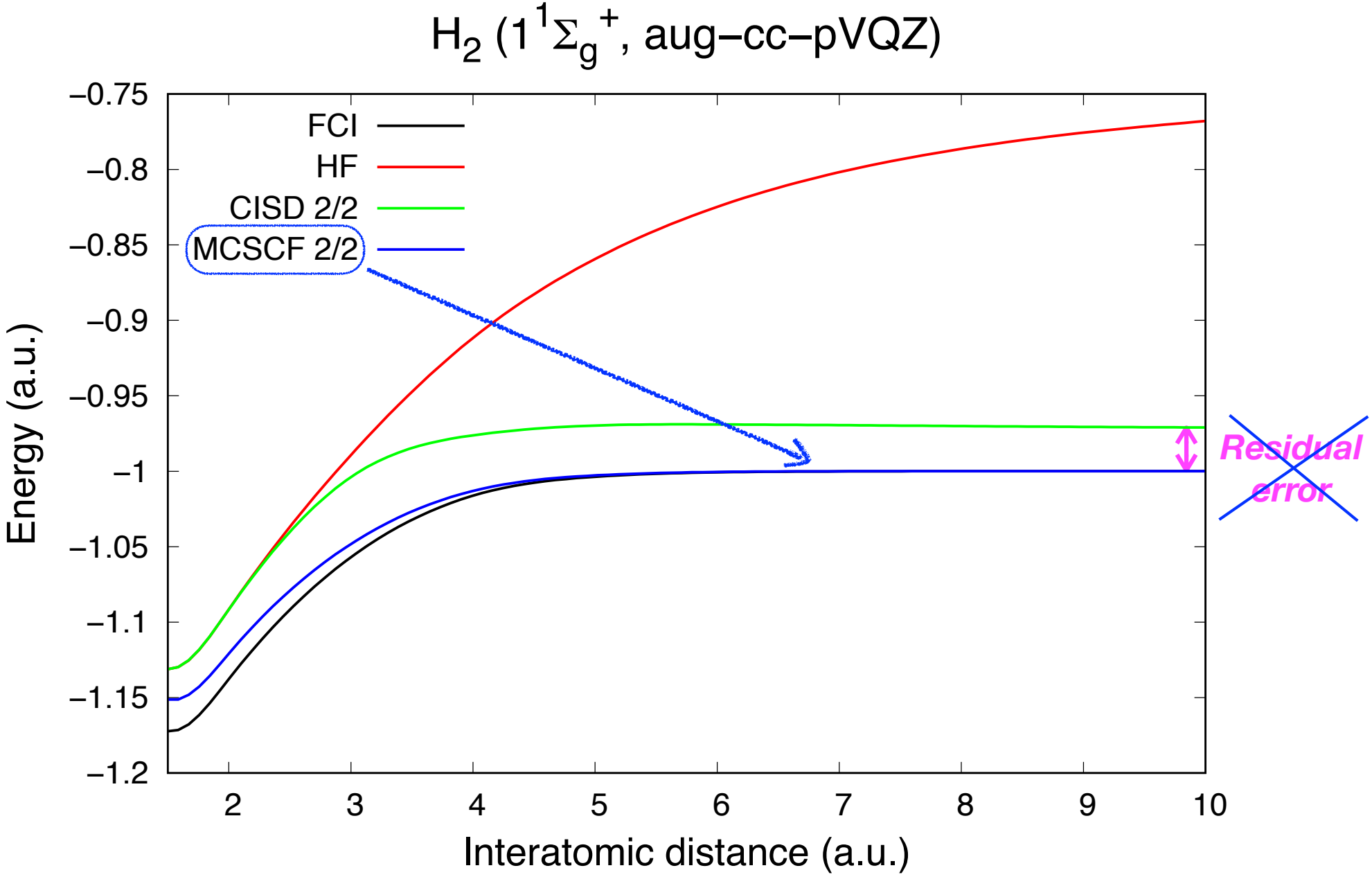
Energy minimisation

(Generalized) ***Brillouin theorem***

At convergence

$$0 = \langle \hat{a}_2^\dagger \hat{a}_1 \Psi \,|\, \hat{H}\Psi \rangle - \langle \hat{a}_1^\dagger \hat{a}_2 \Psi \,|\, \hat{H}\Psi \rangle$$

Dissociation of the hydrogen molecule



Outline

- Strong electron correlation regime

The prototypical hydrogen molecule at dissociation

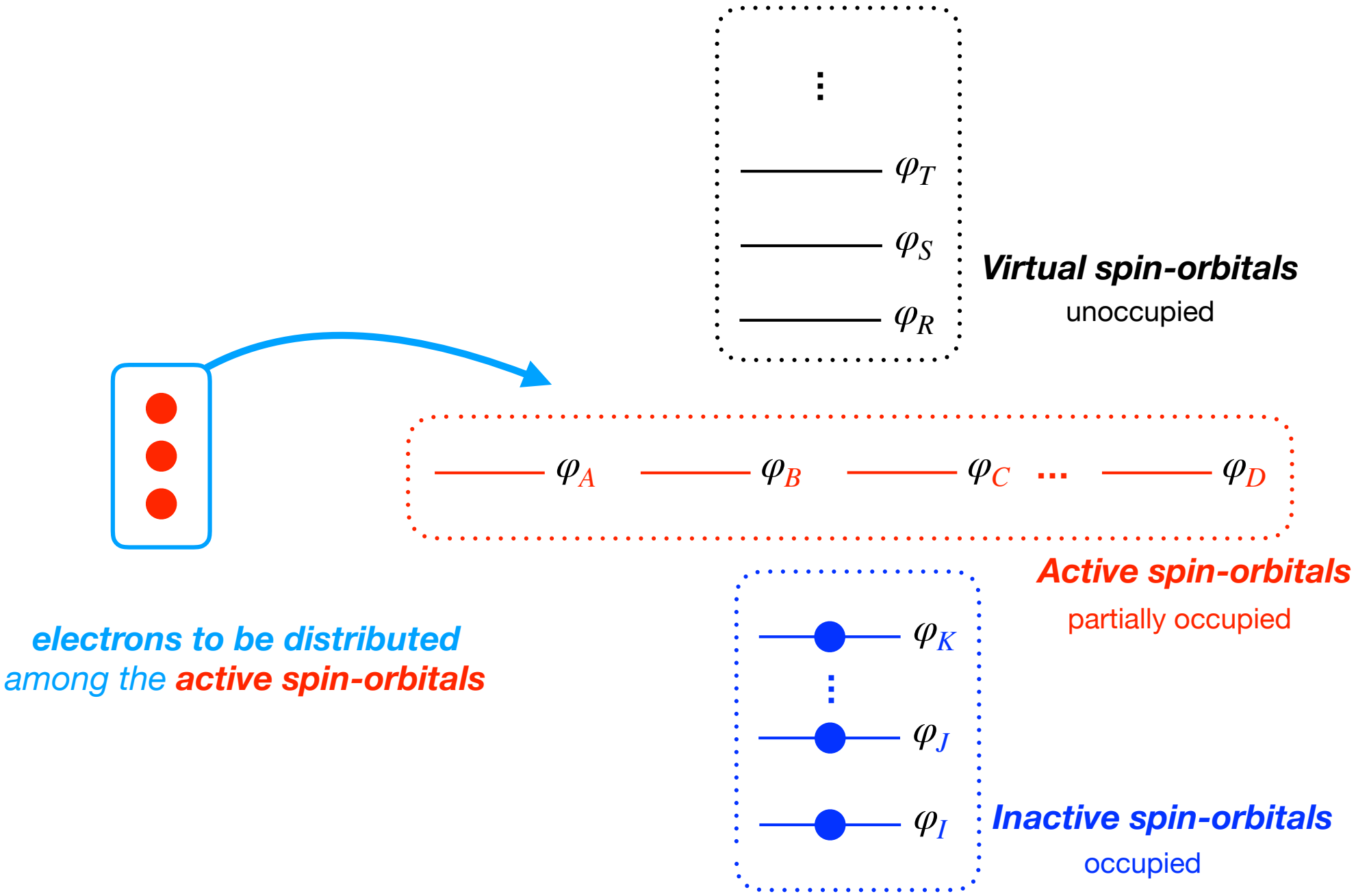
- Orbital rotation in second quantization

Orbital optimisation procedure

- **C**omplete **A**ctive **S**pace **S**elf-**C**onsistent **F**ield and beyond

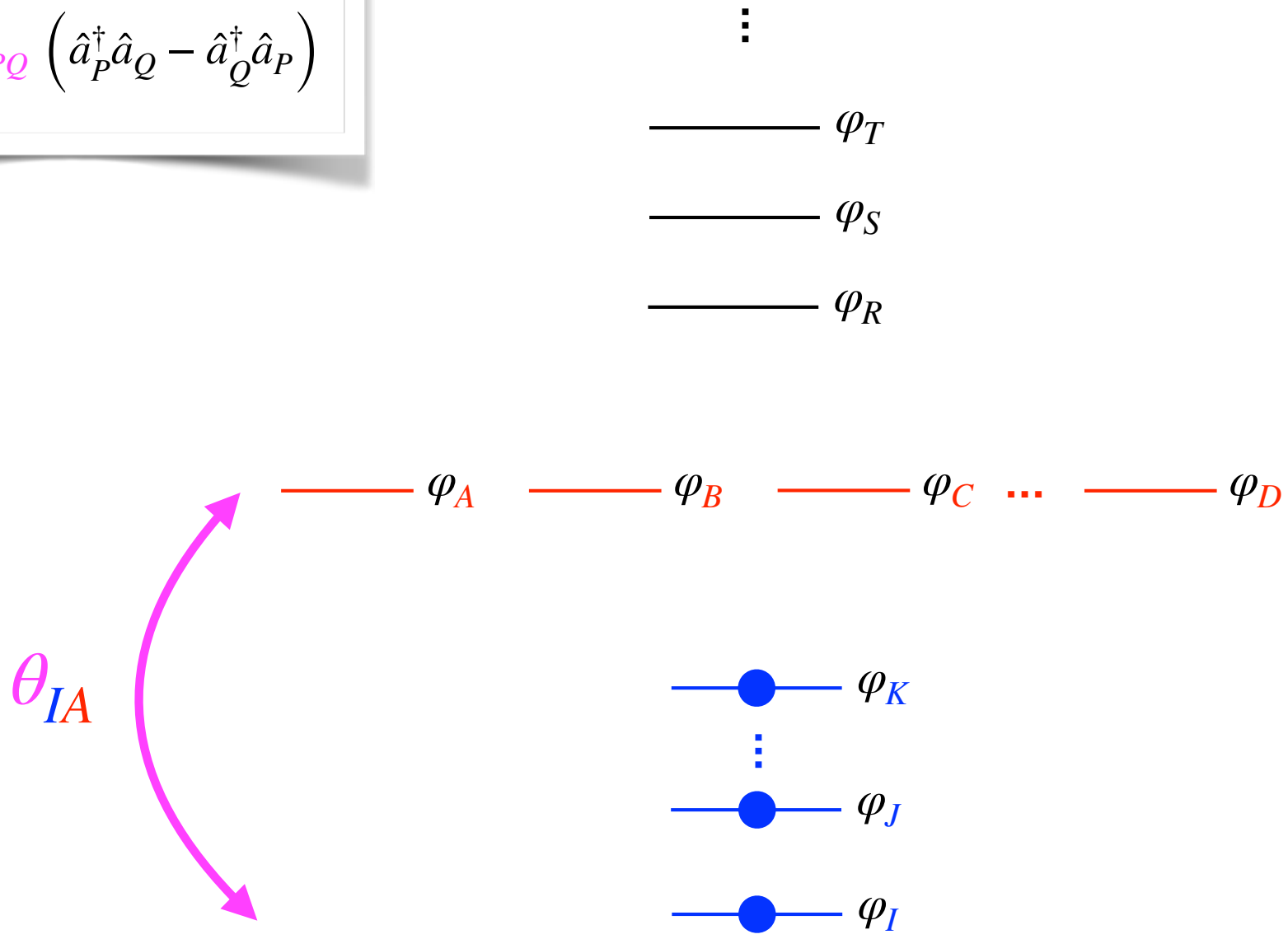
General CASSCF approach, state-averaging,
multi-reference perturbation theory

Multi-Configurational Self-Consistent Field (MCSCF)



Multi-Configurational Self-Consistent Field (MCSCF)

$$\hat{\theta} \equiv \sum_{P<Q} \theta_{PQ} \left(\hat{a}_P^\dagger \hat{a}_Q - \hat{a}_Q^\dagger \hat{a}_P \right)$$



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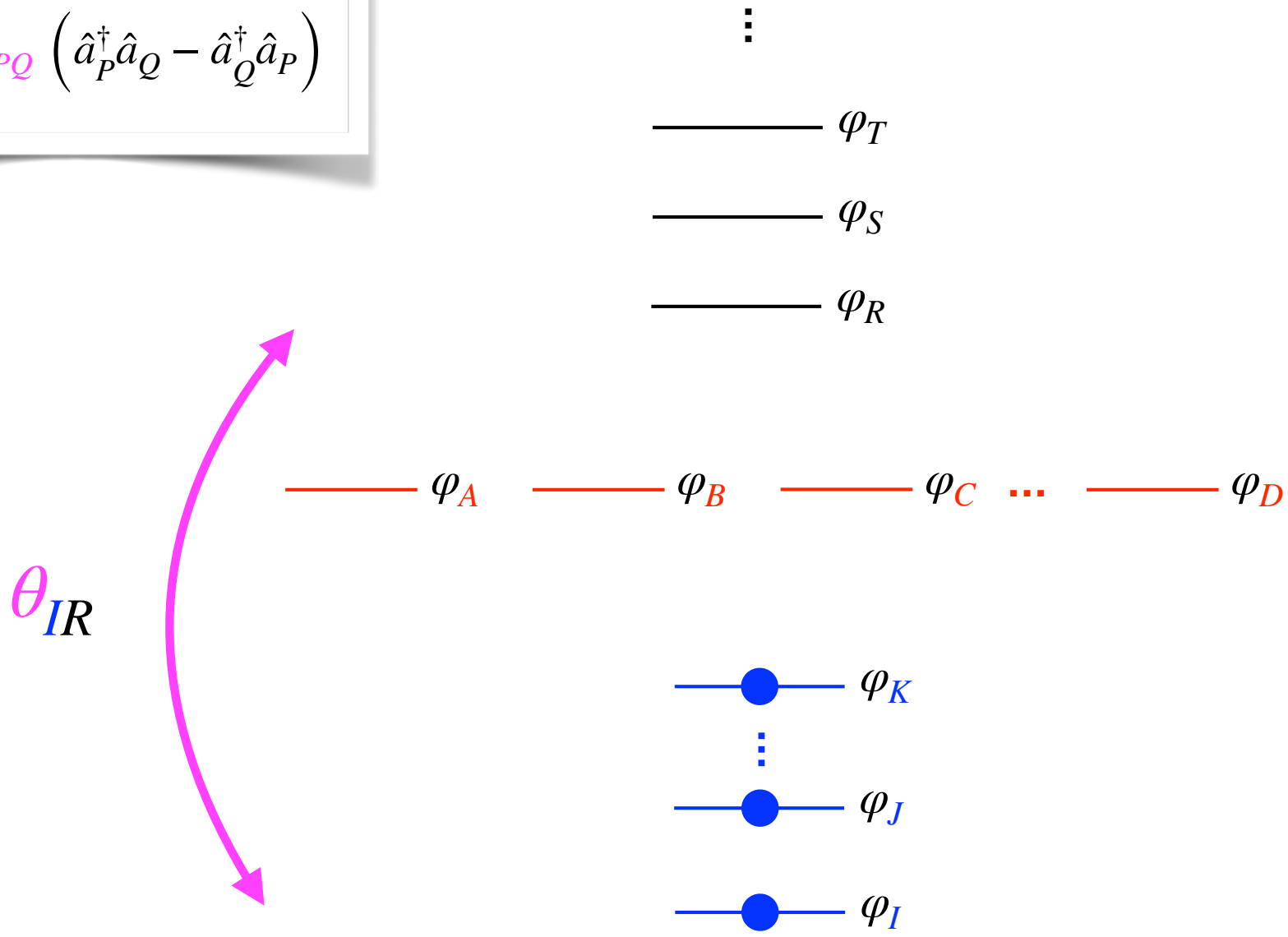

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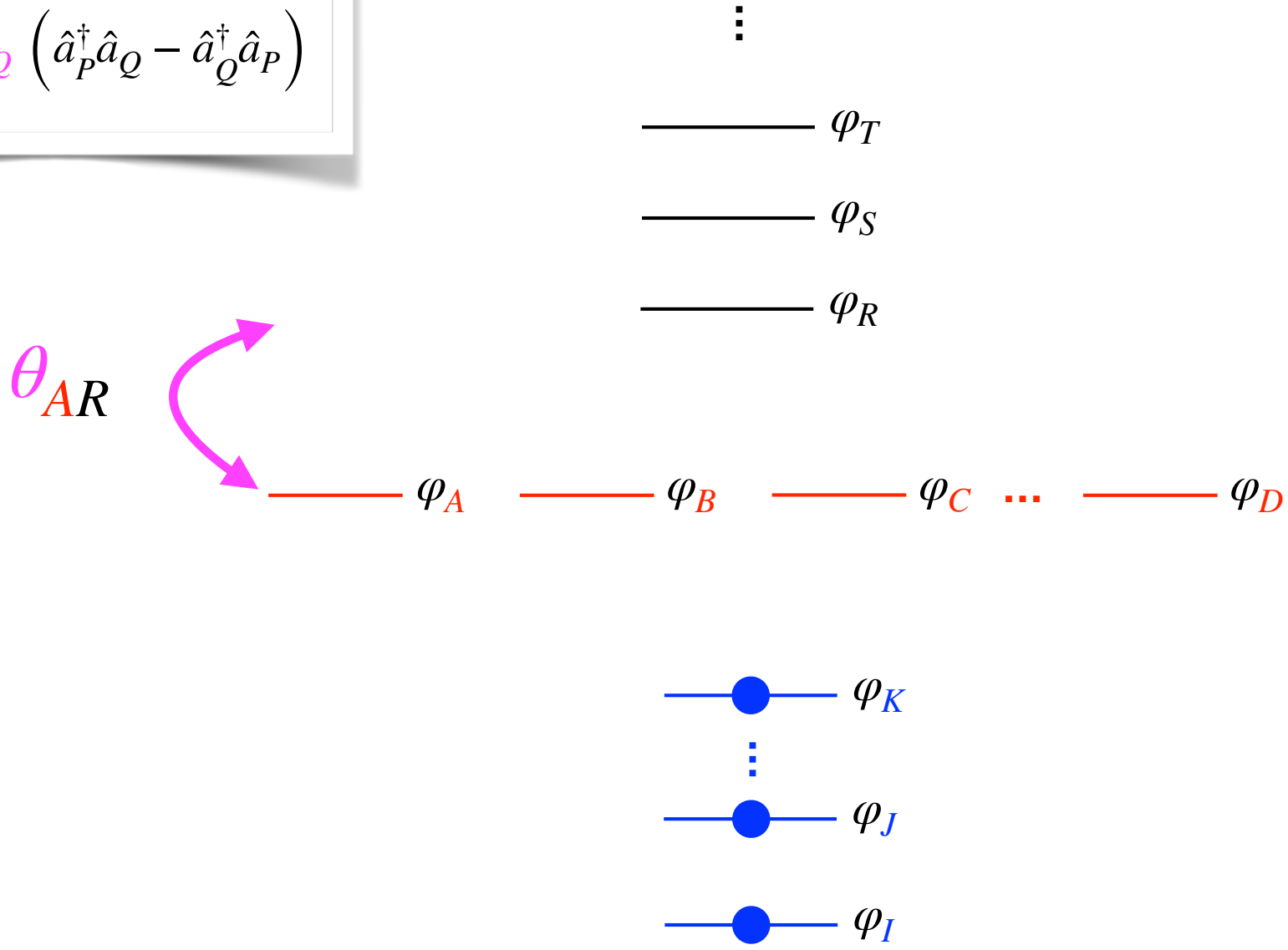
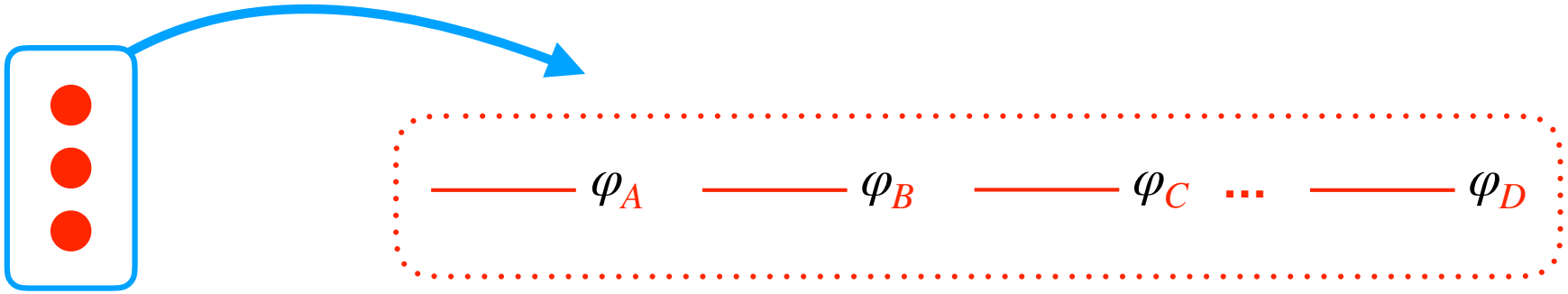
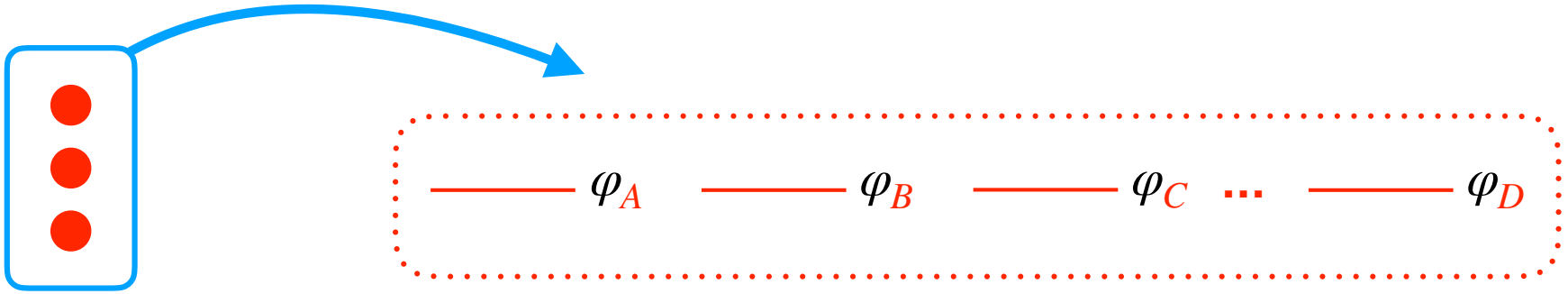


Multi-Configurational Self-Consistent Field (MCSCF)



If *FCI within the active* spin-orbital space: ***Complete Active Space SCF*** (CASSCF)

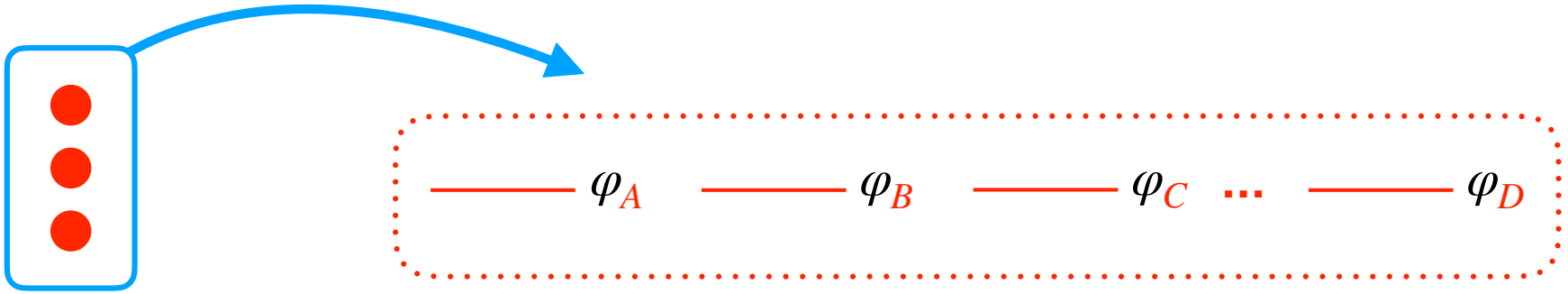
Multi-Configurational Self-Consistent Field (MCSCF)



If *FCI within the active* spin-orbital space: ***Complete Active Space SCF*** (CASSCF)

Several (ground and excited) states can be computed simultaneously

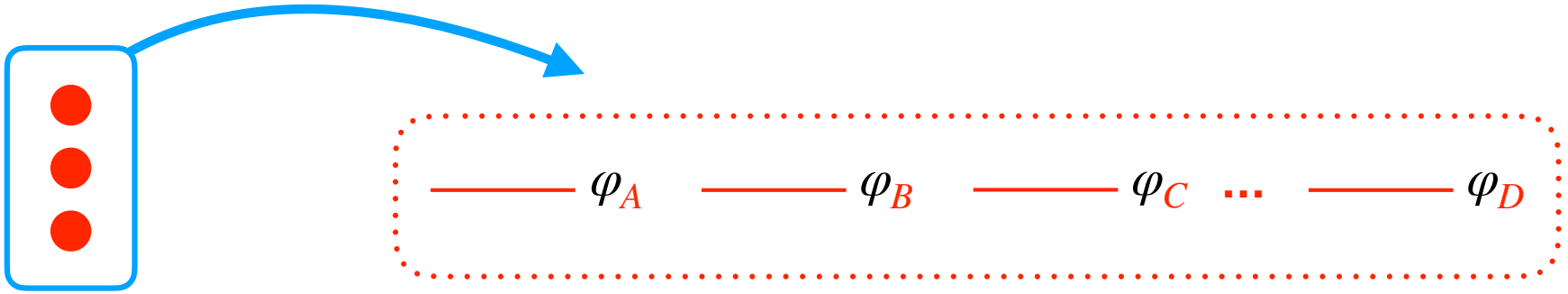
Multi-Configurational Self-Consistent Field (MCSCF)



With the same set of orbitals!

Several (ground and excited) states can be computed ***simultaneously***

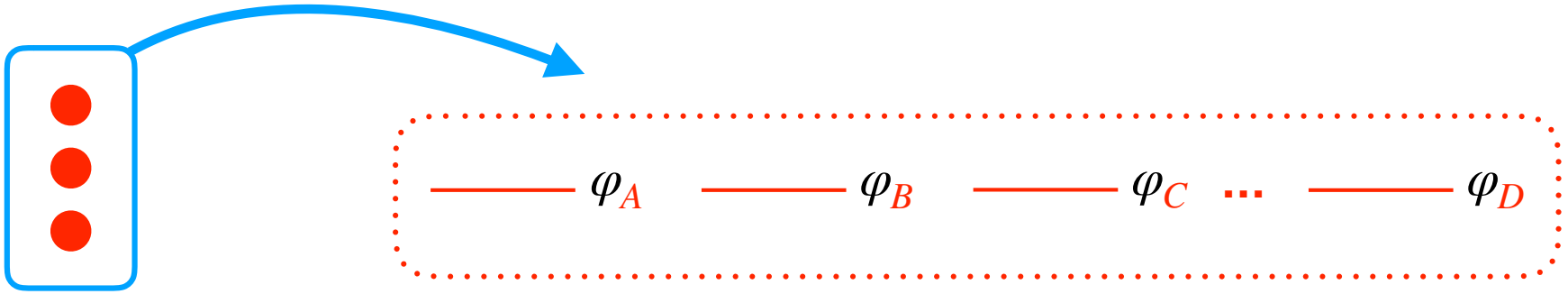
Multi-Configurational Self-Consistent Field (MCSCF)



$$E(\theta) = \sum_{\mathcal{J}} \langle \Psi_{\mathcal{J}} | e^{+\hat{\theta}} \hat{H} e^{-\hat{\theta}} | \Psi_{\mathcal{J}} \rangle$$

Several (ground and excited) states can be computed simultaneously

Multi-Configurational Self-Consistent Field (MCSCF)

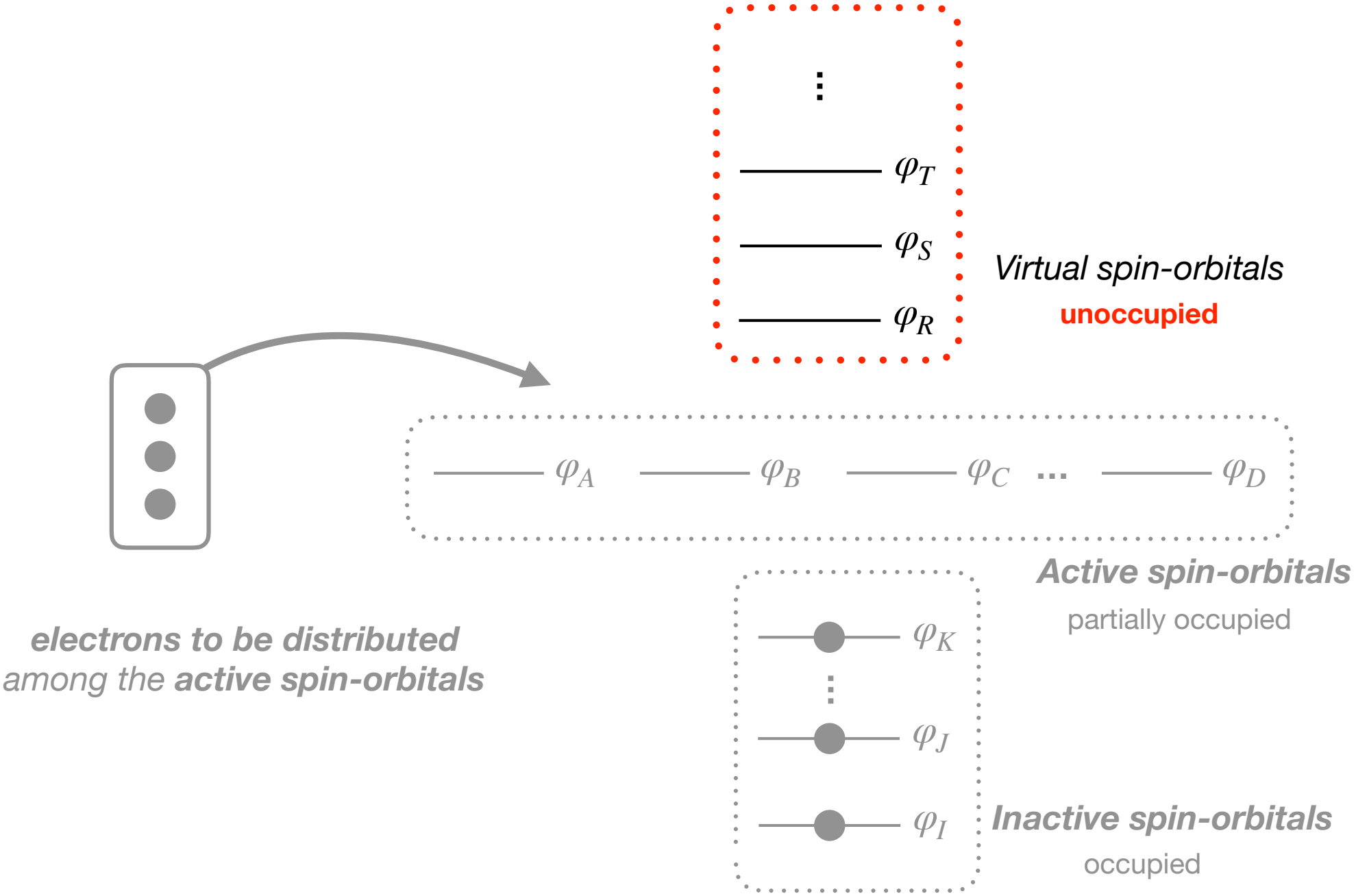


$$E(\theta) = \sum_{\mathcal{J}} \langle \Psi_{\mathcal{J}} | e^{+\hat{\theta}} \hat{H} e^{-\hat{\theta}} | \Psi_{\mathcal{J}} \rangle$$

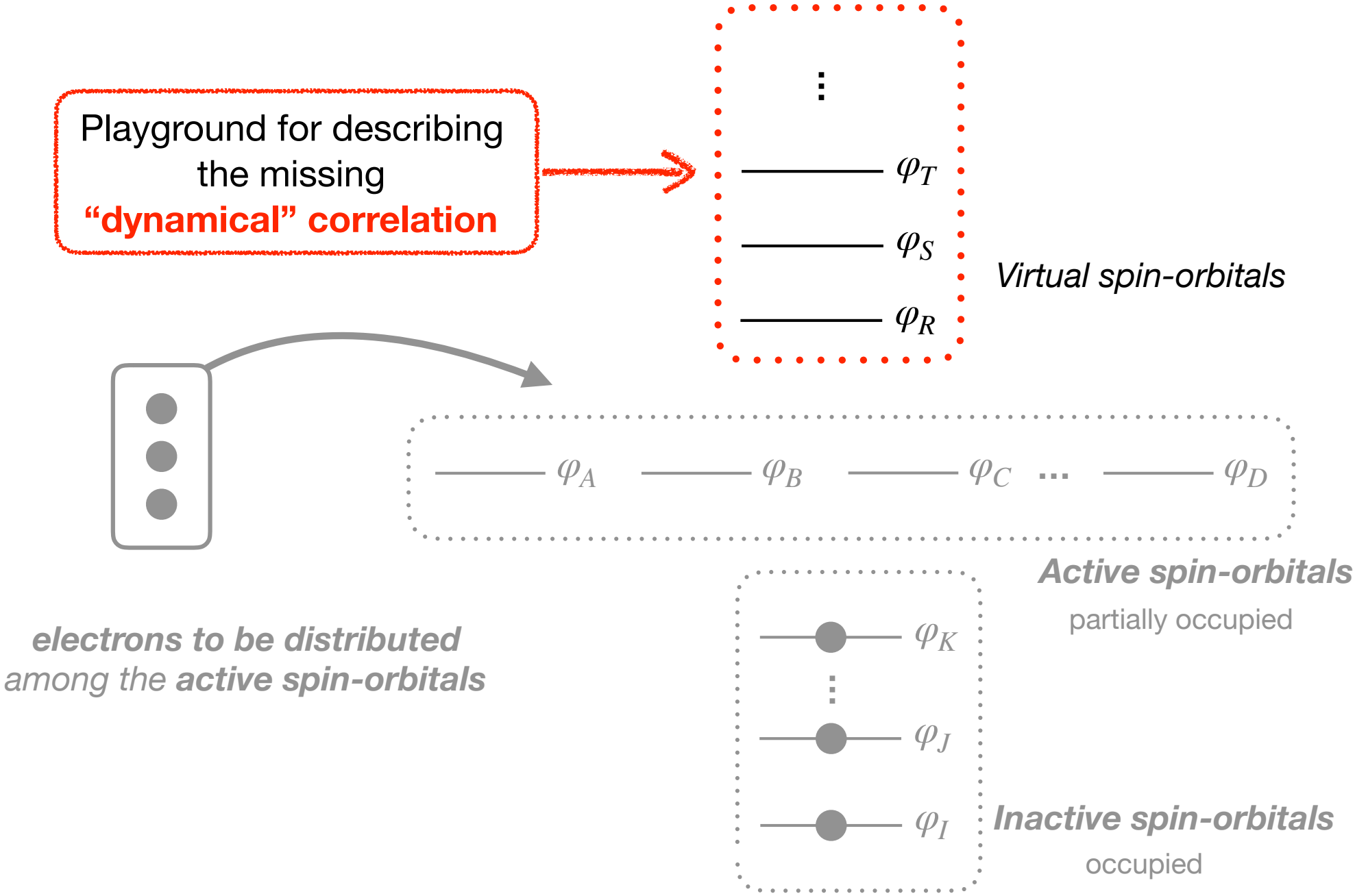
← ***State-averaged*** *CASSCF*

↑ Several (ground and excited) states can be computed simultaneously

Multi-Configurational Self-Consistent Field (MCSCF)



Post-MCSCF treatment



Multi-Reference *Perturbation Theory through second order (MRPT2)*

We know from textbook **perturbation theory** that

$$E \approx E_{\mathrm{MCSCF}} + \sum_{\tilde{\Psi}_i \perp \Psi_{\mathrm{MCSCF}}} \frac{\left| \langle \tilde{\Psi}_i | \hat{H} | \Psi_{\mathrm{MCSCF}} \rangle \right|^2}{E_{\mathrm{MCSCF}} - \tilde{\mathscr{E}}_i}$$

"perturber" with energy $\tilde{\mathscr{E}}_i$

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Clearly identified in *single reference* ***MP2****: double excitation*

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~~***Clearly identified in** single reference **MP2**: double excitation*~~

Not in a multi-reference context!

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"perturber" with energy $\tilde{\mathscr{E}}_i$

You can use ***CASPT2***[a]*, or* ***NEVPT2***[b]*, or* ***GVVPT2***[c]*, or …*

[a] *K. Andersson, P. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Phys. Chem.* ***94****, 5483 (1990).*

[b] *C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, J. Chem. Phys.* ***114****, 10252 (2001).*

[c] *Y. G. Khait, J. Song, and M. R. Hoffmann, J. Chem. Phys.* ***117****, 4133 (2002).*

Multi-Reference *Perturbation Theory through second order (MRPT2)*

We know from textbook perturbation theory that

$$E \approx E_{\mathrm{MCSCF}} + \sum_{\tilde{\Psi}_i \perp \Psi_{\mathrm{MCSCF}}} \frac{\left| \langle \tilde{\Psi}_i | \hat{H} | \Psi_{\mathrm{MCSCF}} \rangle \right|^2}{E_{\mathrm{MCSCF}} - \tilde{\mathscr{E}}_i}$$

$\neq 0$

Contributing perturbers $\tilde{\Psi}_i$ ***overlap with*** $\hat{H}\Psi_{\mathrm{MCSCF}}$

N-Electron Valence state Perturbation Theory (NEVPT2)

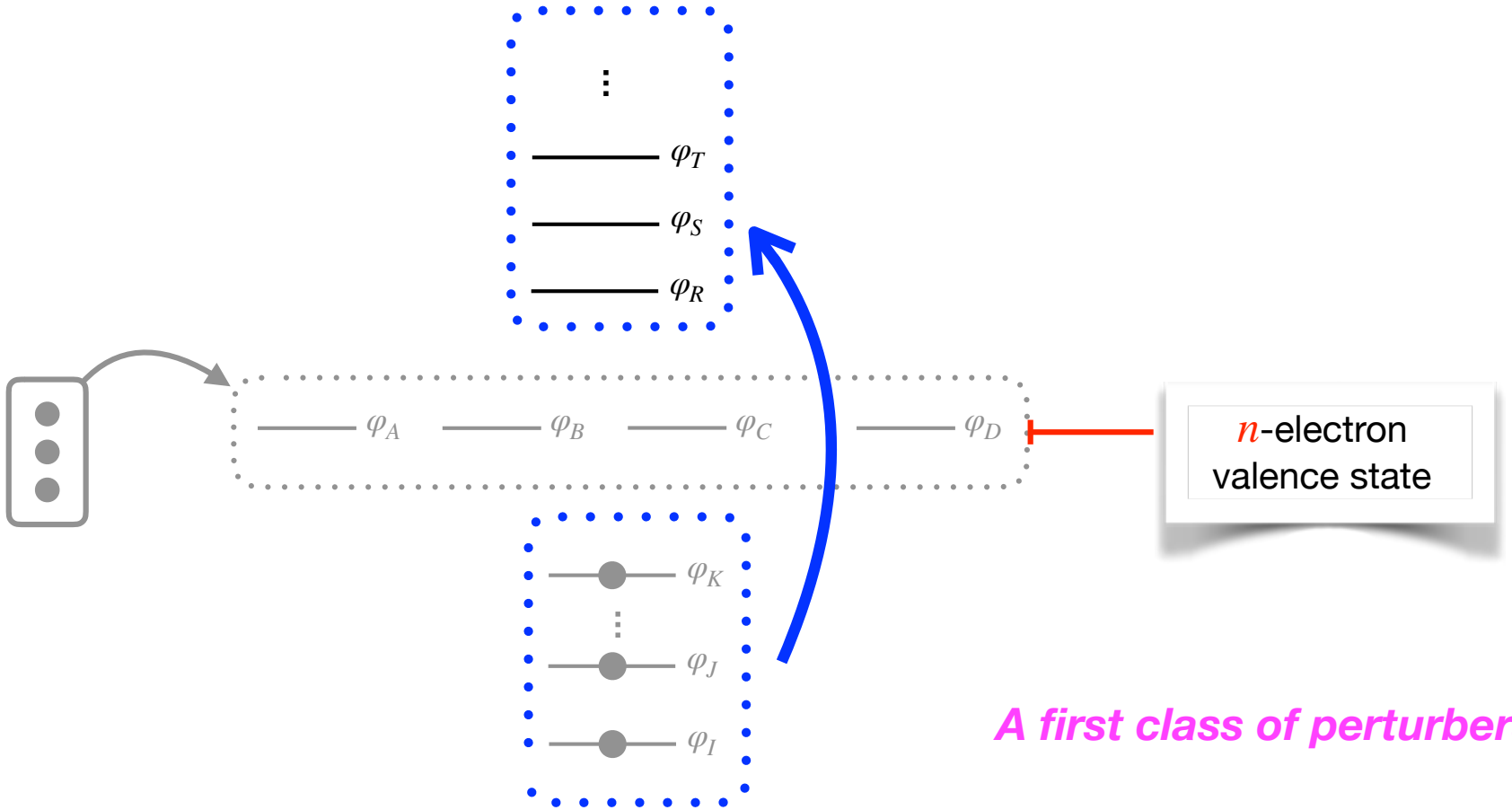
$$\hat{H}\,|\Psi_{\mathrm{MCSCF}}\rangle = \left(\sum_{PQ} h_{PQ} \overbrace{\hat{a}_P^\dagger \hat{a}_Q}^{\text{Singles}} + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q \,|\, \hat{g} \,|\, \varphi_R \varphi_S \rangle \overbrace{\hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R}^{\text{Singles and doubles}} \right) |\Psi_{\mathrm{MCSCF}}\rangle$$

N-Electron Valence state Perturbation Theory (NEVPT2)

$$\hat{H}\,|\Psi_{\mathrm{MCSCF}}\rangle = \left(\sum_{PQ} h_{PQ}\hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2}\sum_{PQRS} \langle \varphi_P\varphi_Q\,|\,\hat{g}\,|\,\varphi_R\varphi_S\rangle\, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R \right) |\Psi_{\mathrm{MCSCF}}\rangle$$

Singles

Singles and doubles



A first class of perturbers

N-Electron Valence state Perturbation Theory (NEVPT2)

$$\hat{H}\,|\Psi_{\mathrm{MCSCF}}\rangle = \left(\sum_{PQ} h_{PQ}\hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2}\sum_{PQRS} \langle \varphi_P\varphi_Q\,|\,\hat{g}\,|\,\varphi_R\varphi_S\rangle\, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R \right) |\Psi_{\mathrm{MCSCF}}\rangle$$

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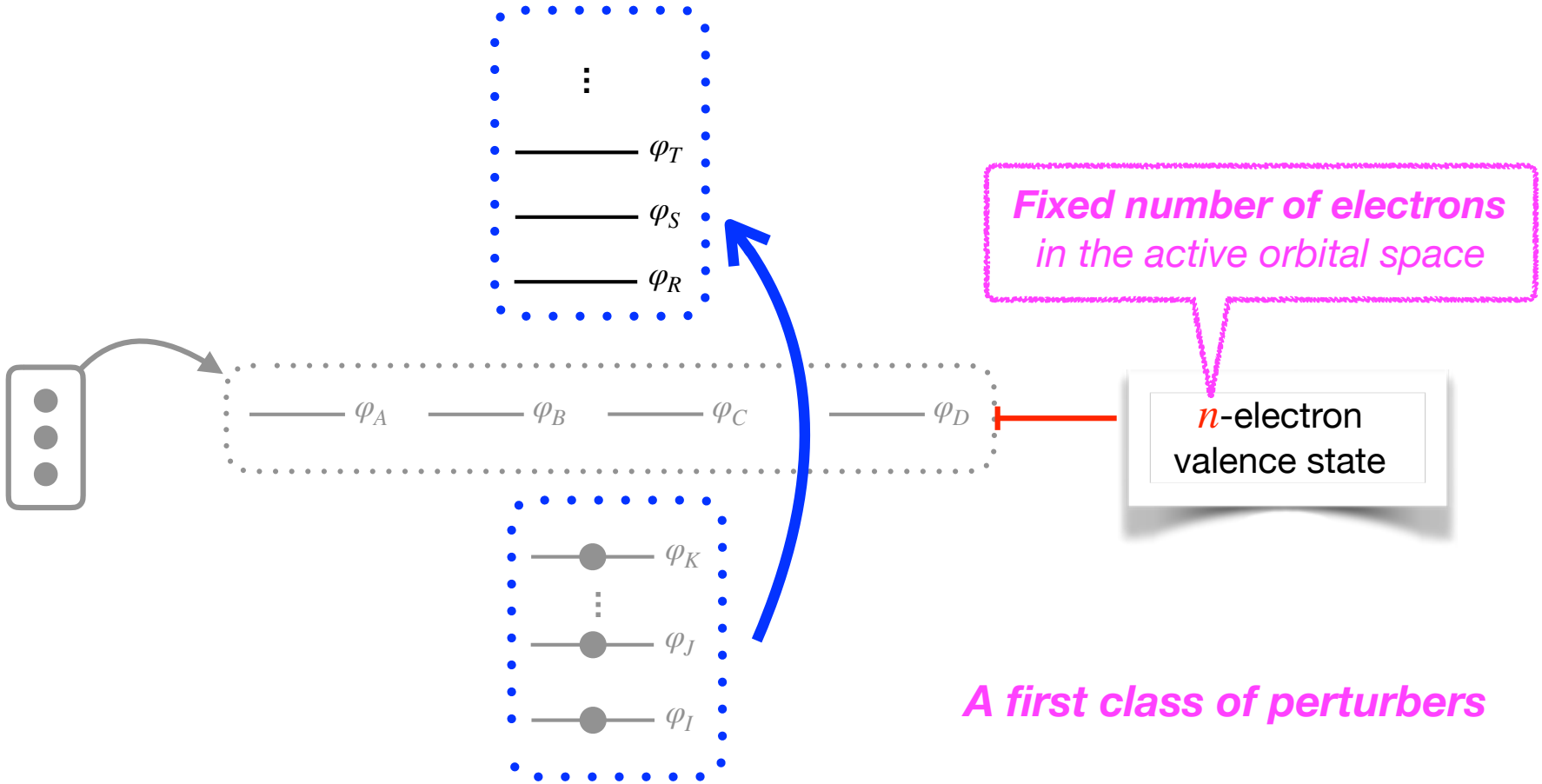

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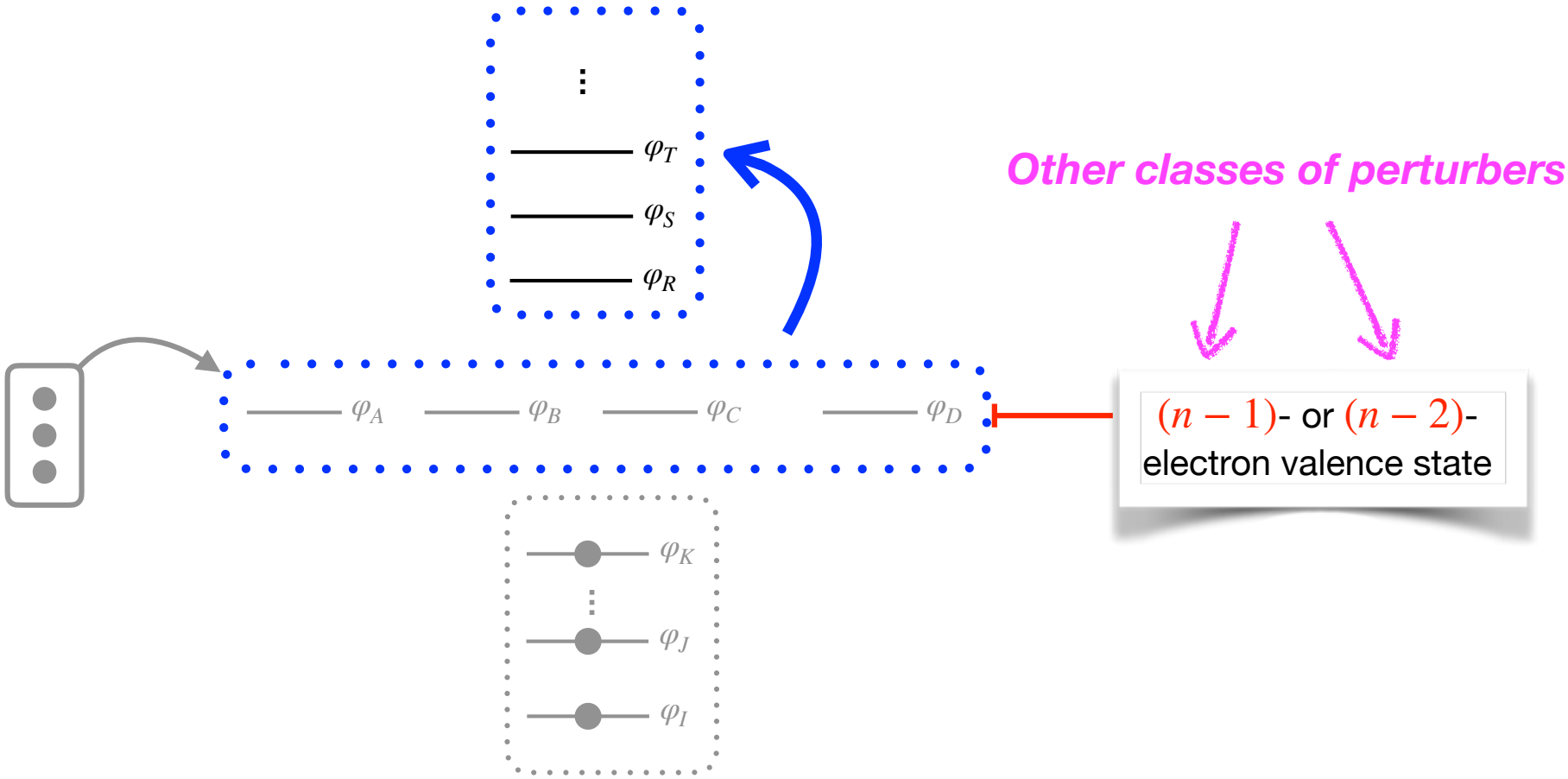

Dissociation of the hydrogen molecule