Multi-Configurational Self-Consistent Field:
An introduction to strong correlation in quantum chemistry

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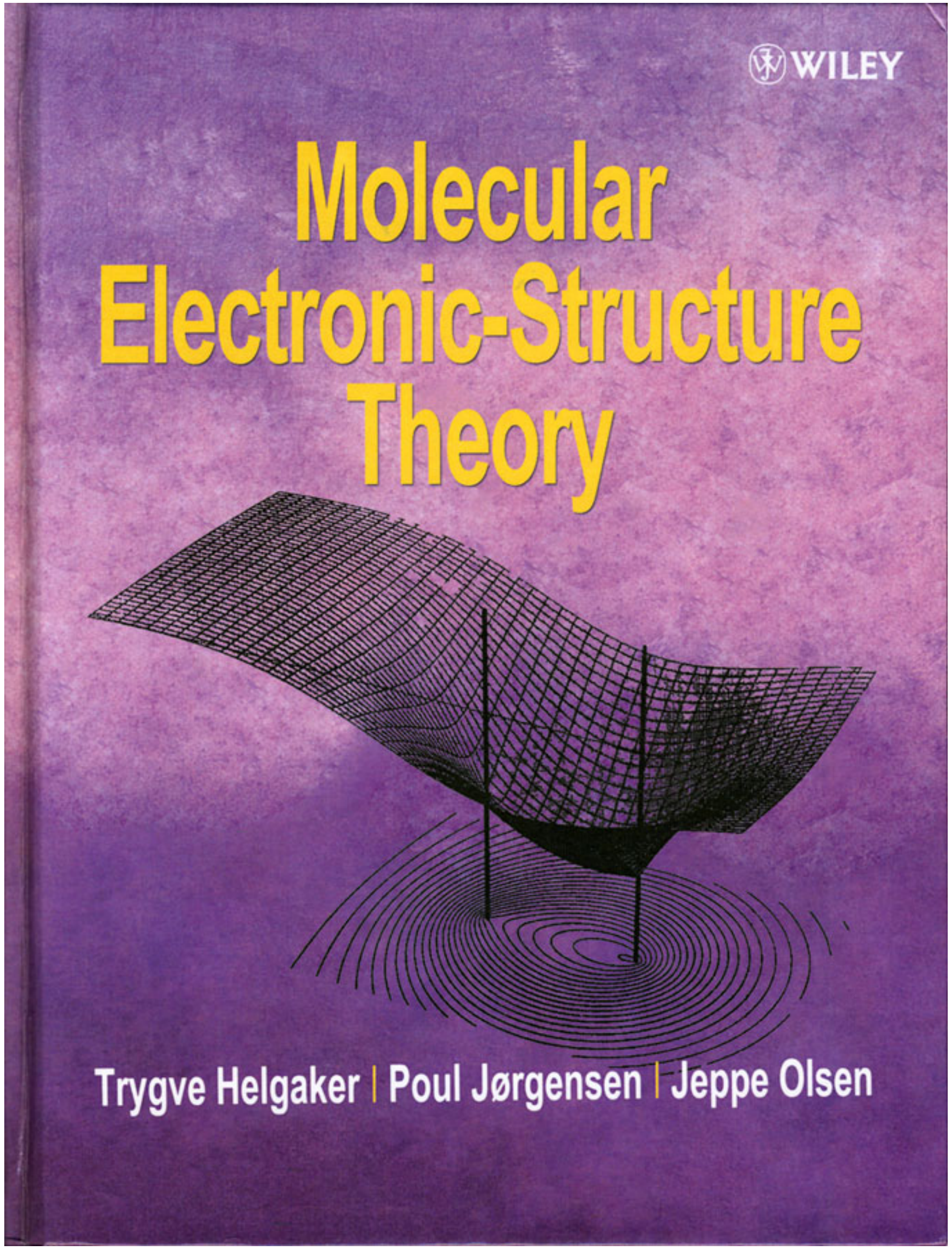
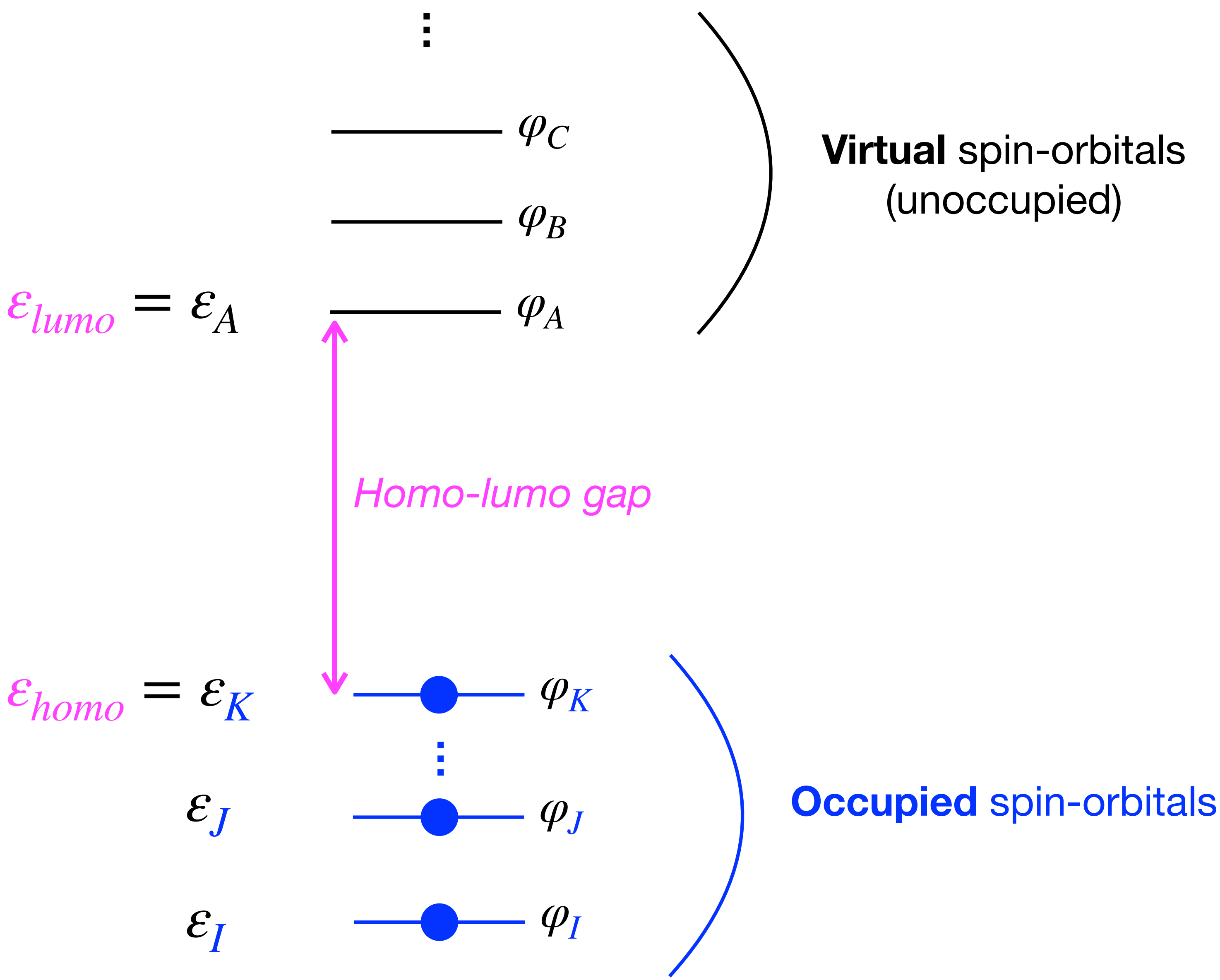
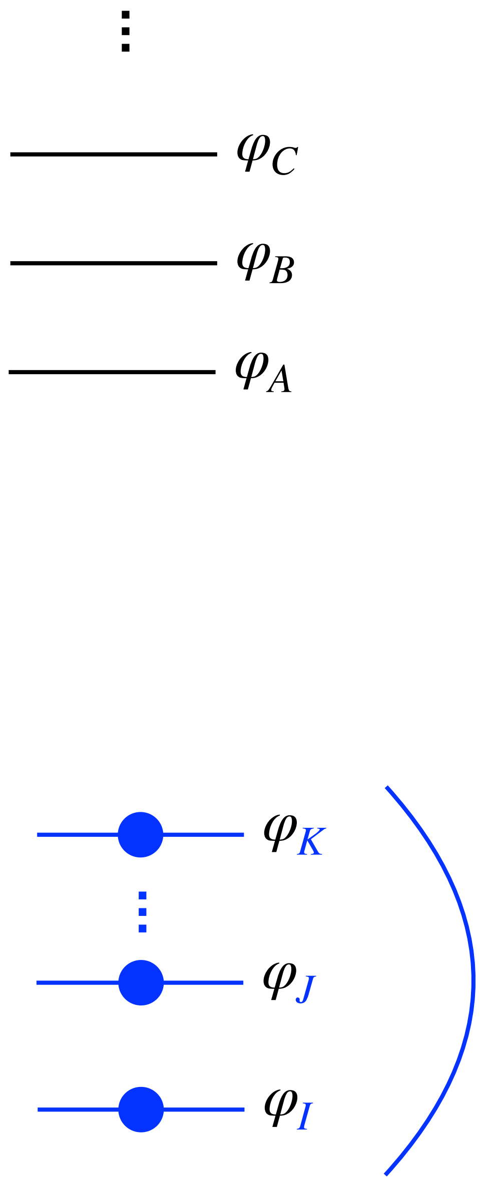
Textbook


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

Hartree-Fock (or KS-DFT) single-configuration picture

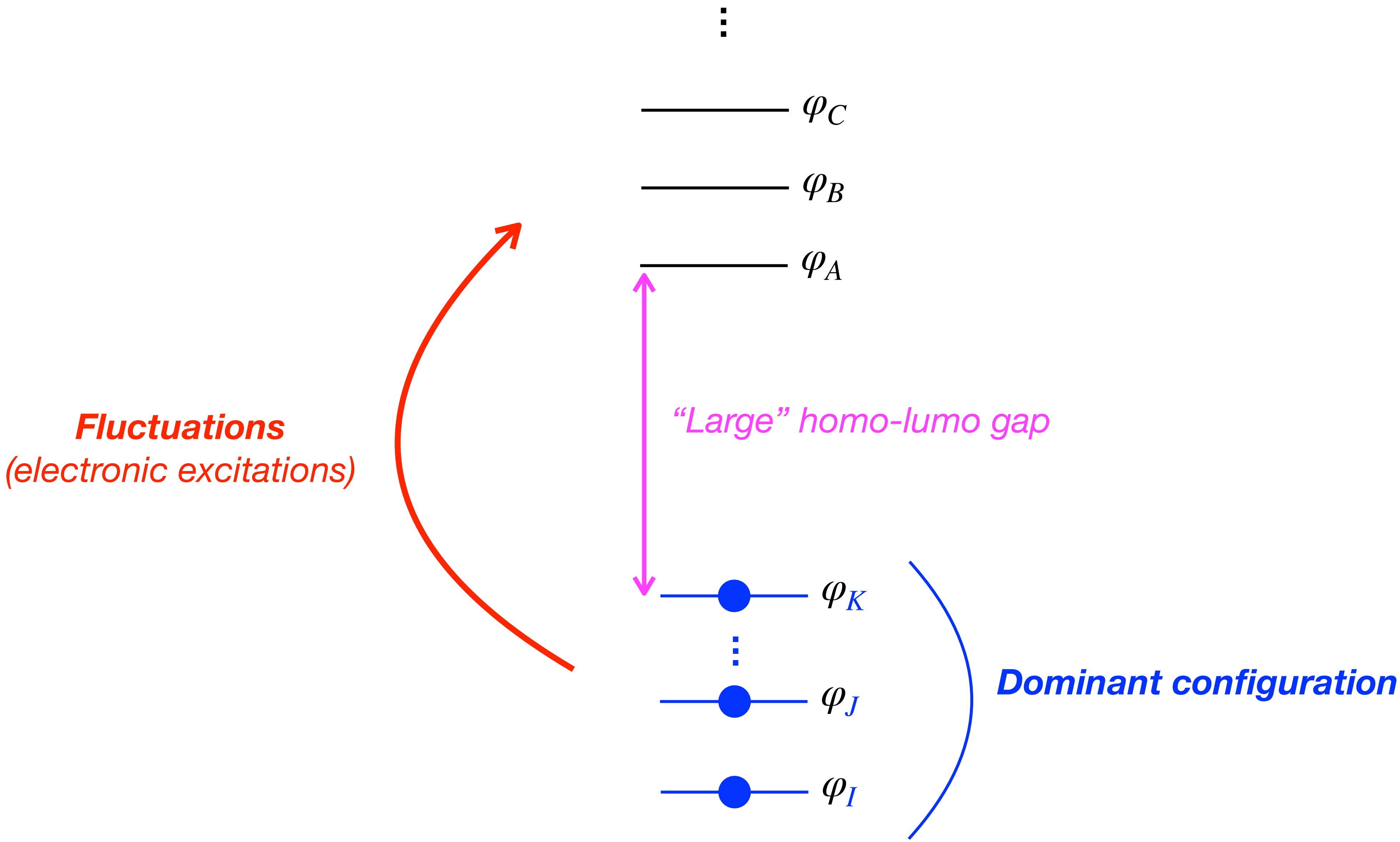


"dynamical" electron correlation

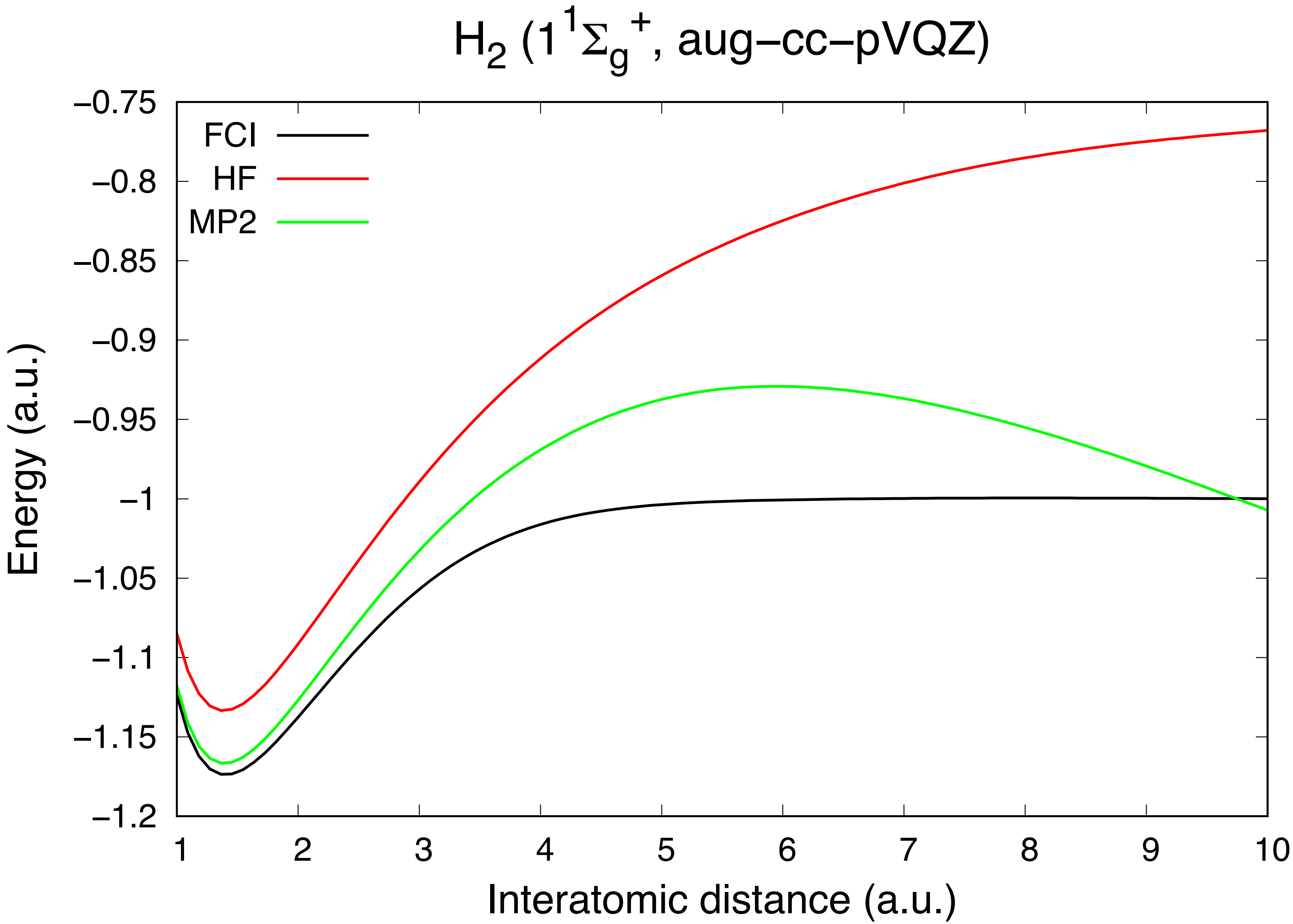


Does ***not*** provide an
exact ground-state
solution to the
Schrödinger equation

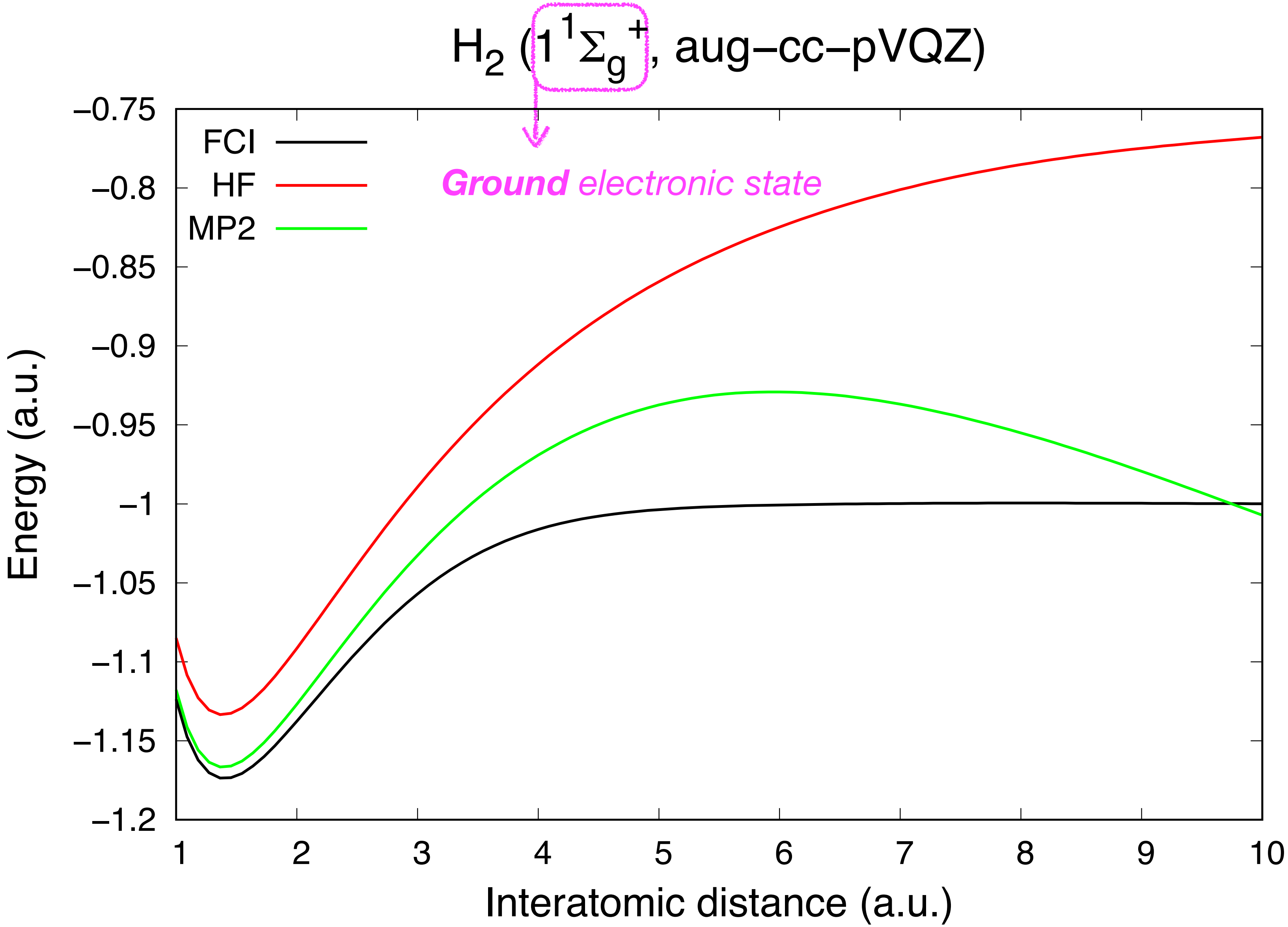
“dynamical” electron correlation



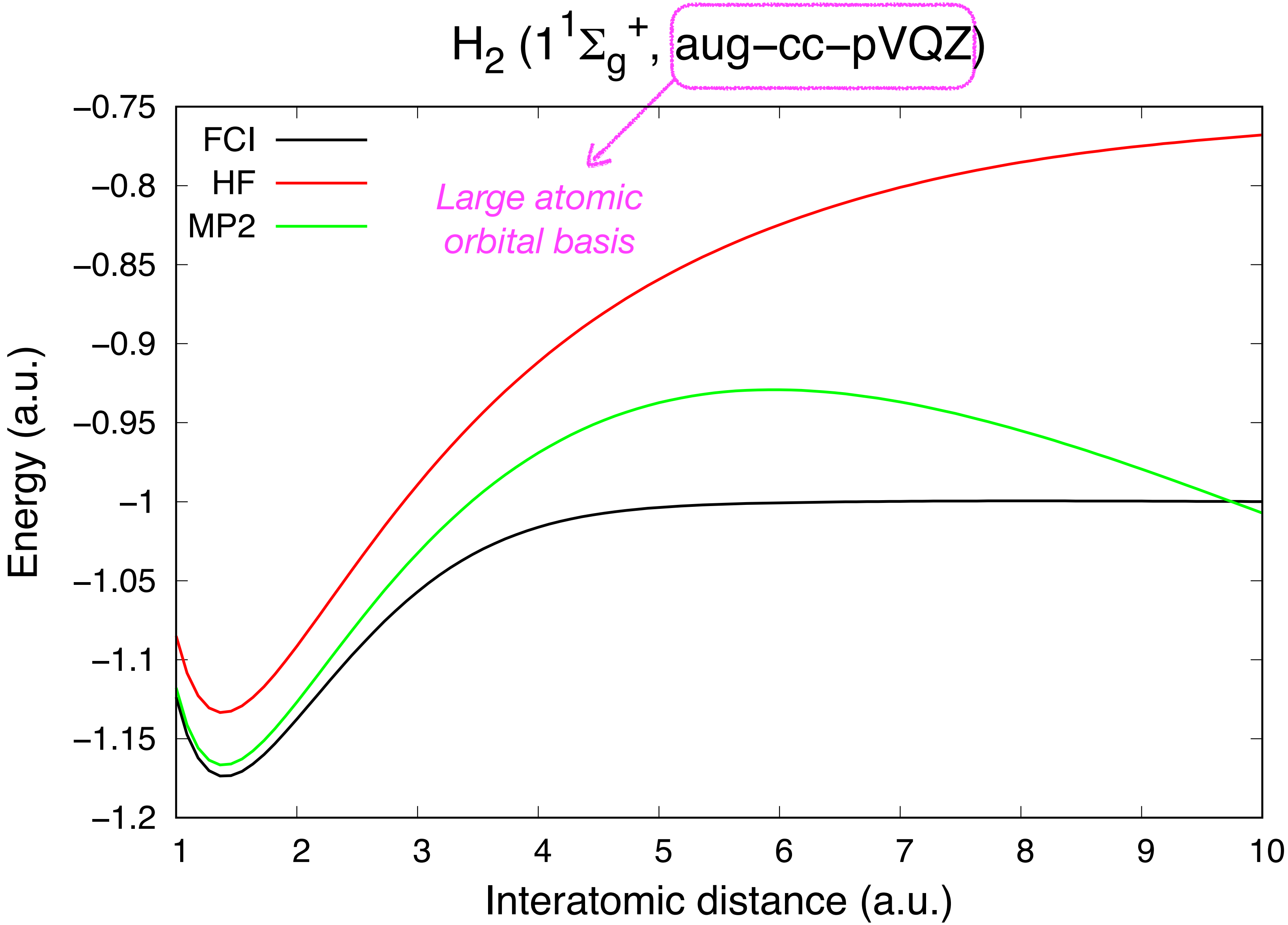
Potential energy curve of the hydrogen molecule



Potential energy curve of the hydrogen molecule



Potential energy curve of the hydrogen molecule



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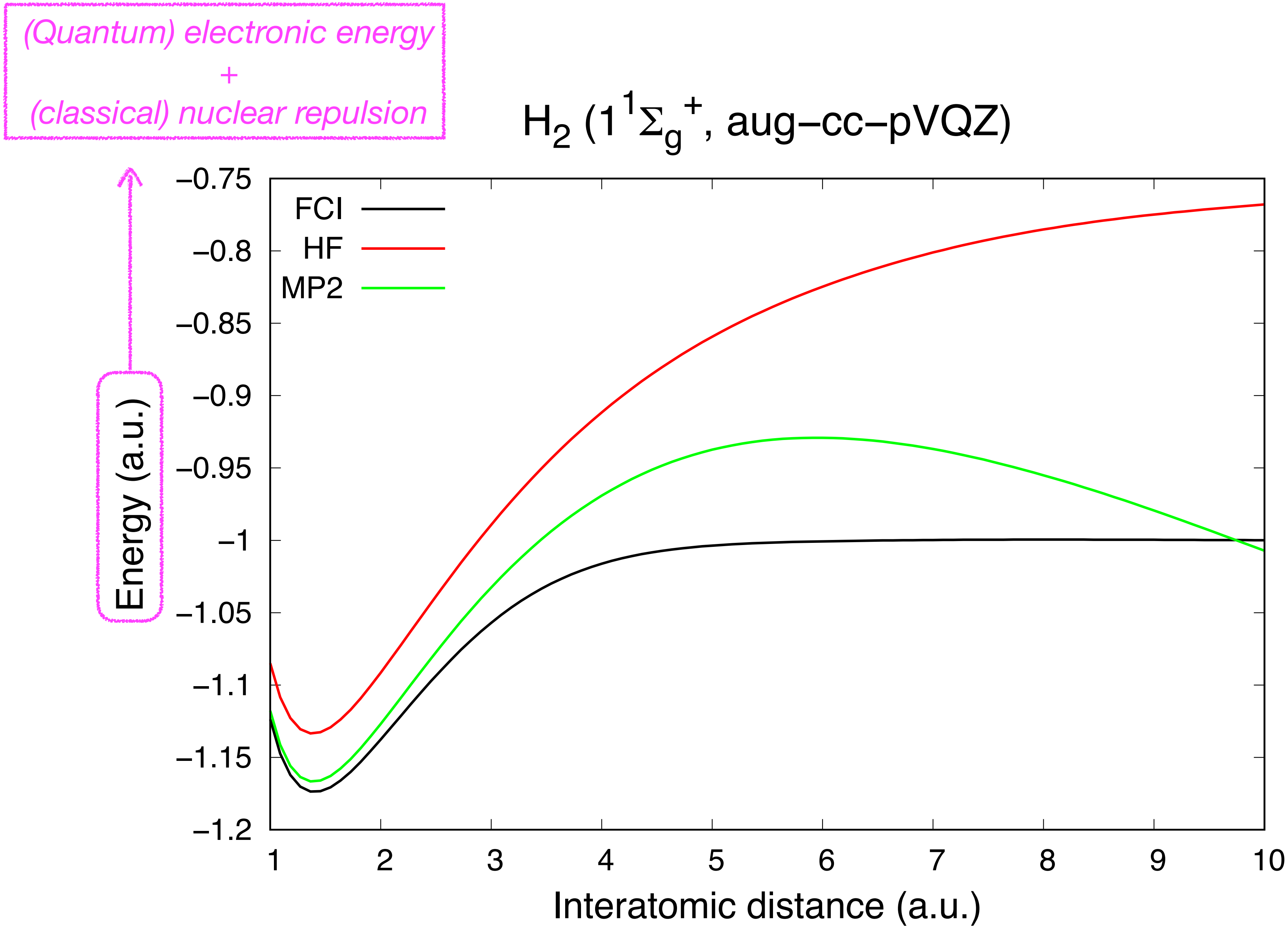
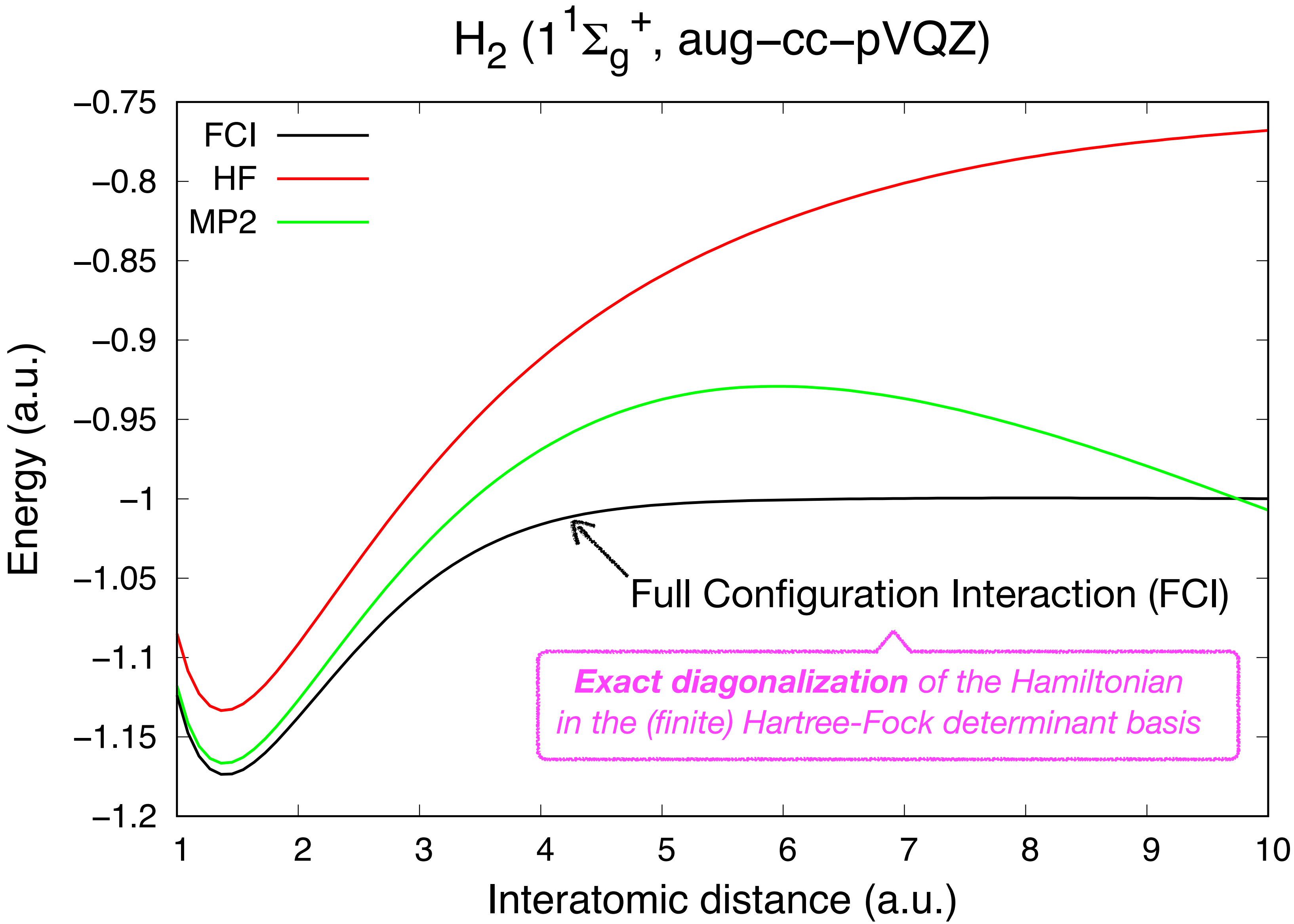
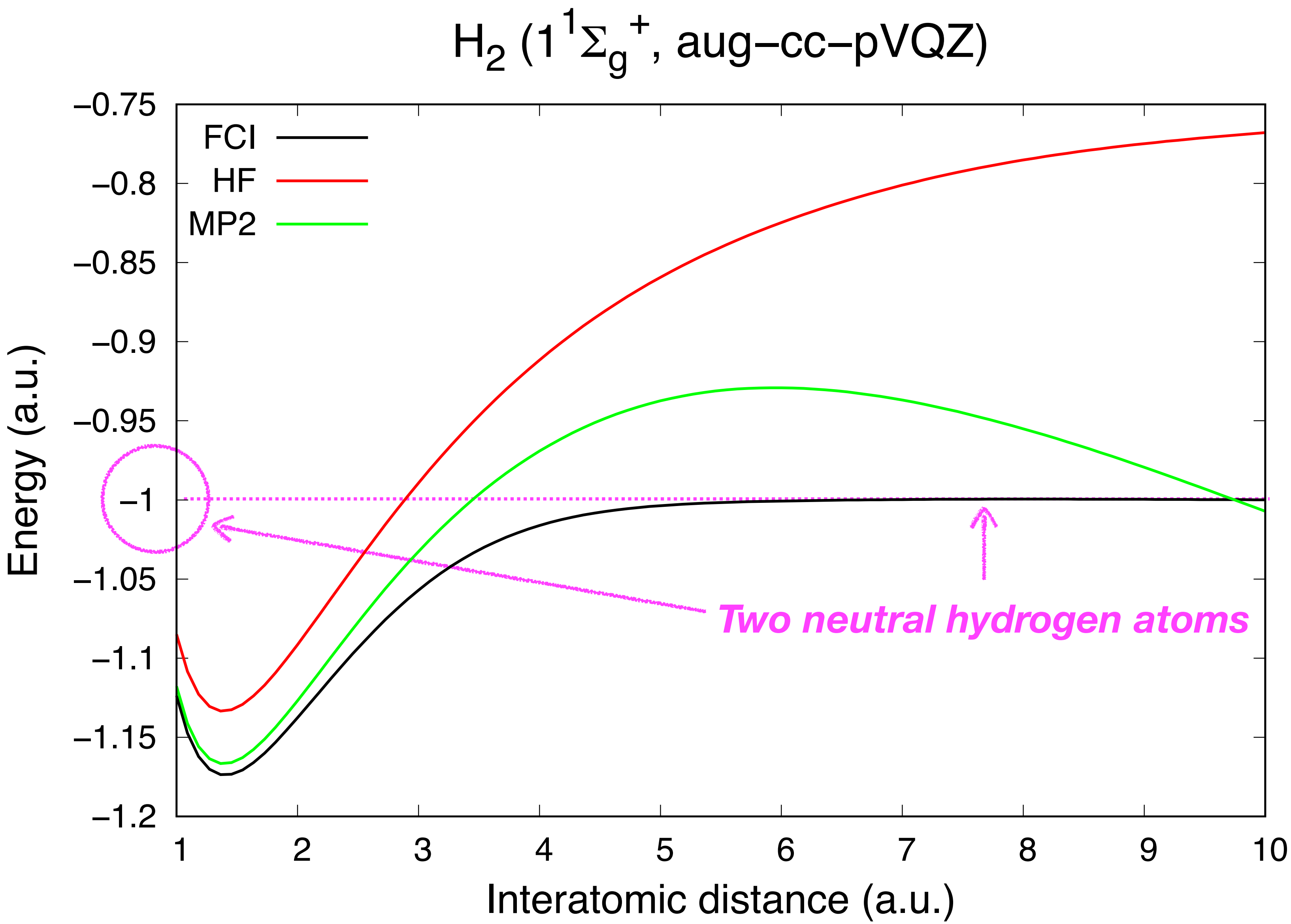


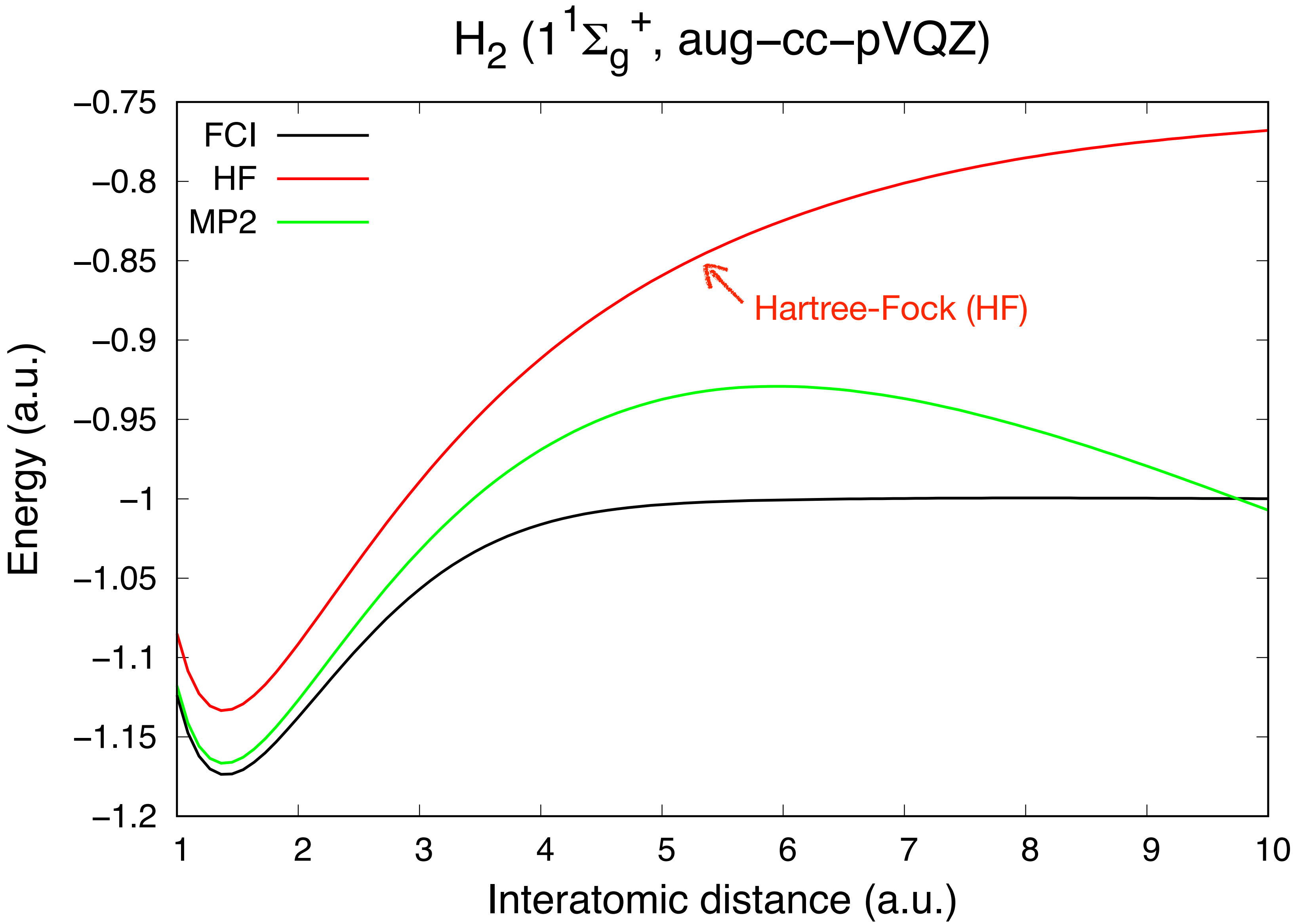
Potential energy curve of the hydrogen molecule



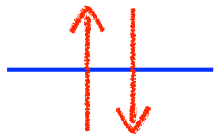
Potential energy curve of the hydrogen molecule



Potential energy curve of the hydrogen molecule



(Restricted) HF wave function of the hydrogen molecule

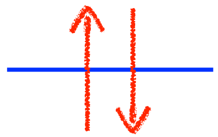


$\varphi_{1\sigma_g}$ Bonding orbital

$$\Phi^{HF}(X_1, X_2) = \frac{1}{\sqrt{2}}\Big(\varphi_{1\sigma_g,\alpha}(X_1)\varphi_{1\sigma_g,\beta}(X_2) - \varphi_{1\sigma_g,\alpha}(X_2)\varphi_{1\sigma_g,\beta}(X_1)\Big)$$

$$= \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}}\Big(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\Big)$$

(Restricted) HF wave function of the hydrogen molecule

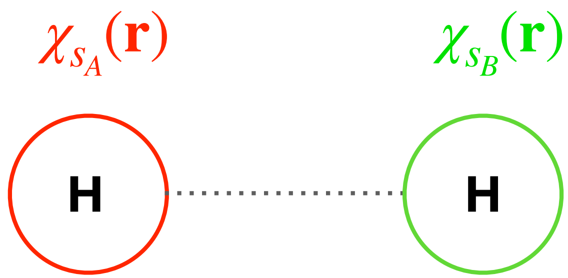


$\varphi_{1\sigma_g}$ Bonding orbital

$$\Phi^{HF}(X_1, X_2) = \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g,\alpha}(X_1)\varphi_{1\sigma_g,\beta}(X_2) - \varphi_{1\sigma_g,\alpha}(X_2)\varphi_{1\sigma_g,\beta}(X_1)\right)$$

$$= \boxed{\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)} \times \frac{1}{\sqrt{2}}\left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right)$$

(Restricted) HF wave function of the stretched hydrogen molecule in a minimal basis



Bonding orbital

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

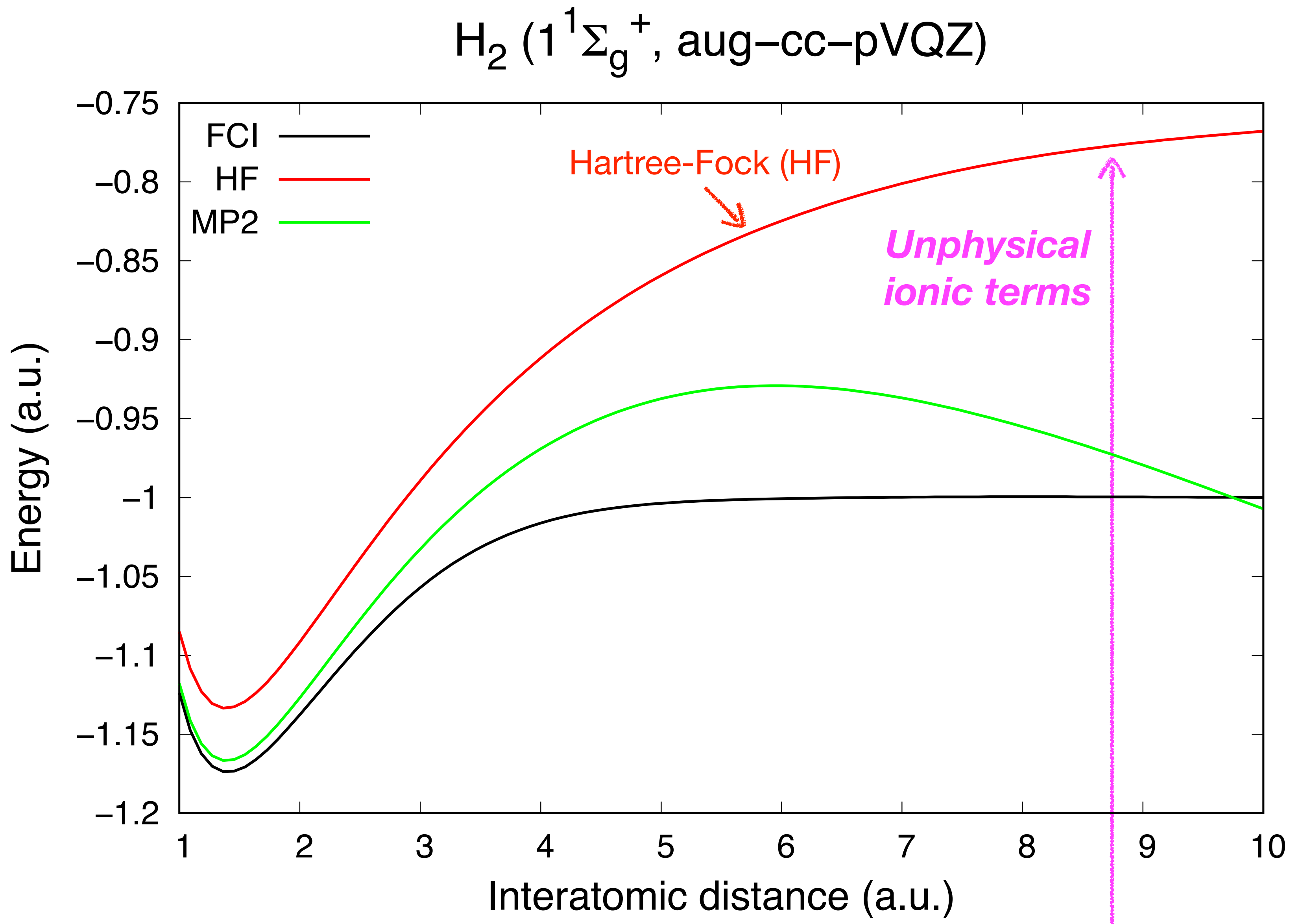
$$= \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}}\left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right)$$

(Restricted) HF wave function of the stretched hydrogen molecule in a minimal basis

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

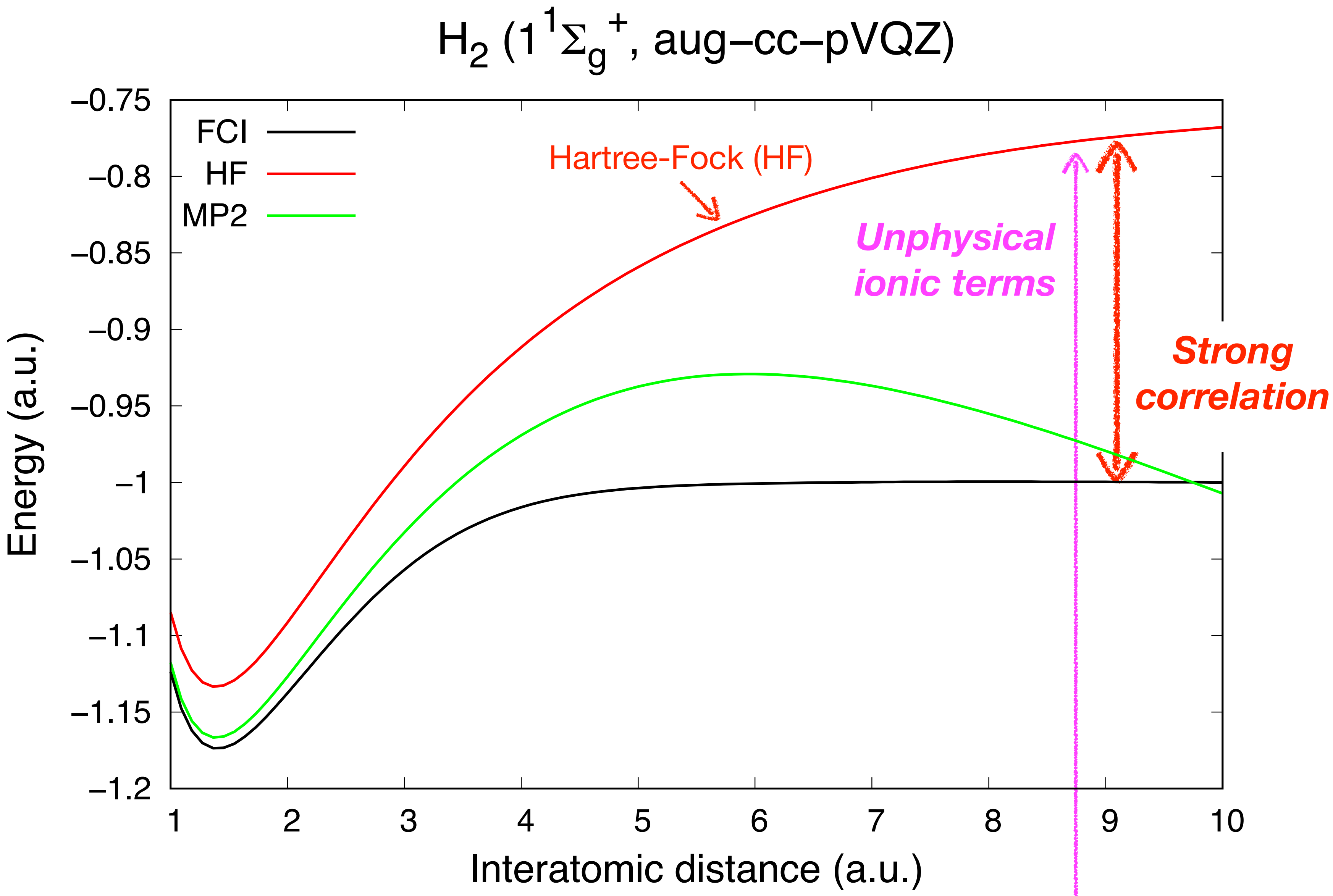
$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

$$= \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) \times \frac{1}{\sqrt{2}}\left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right)$$

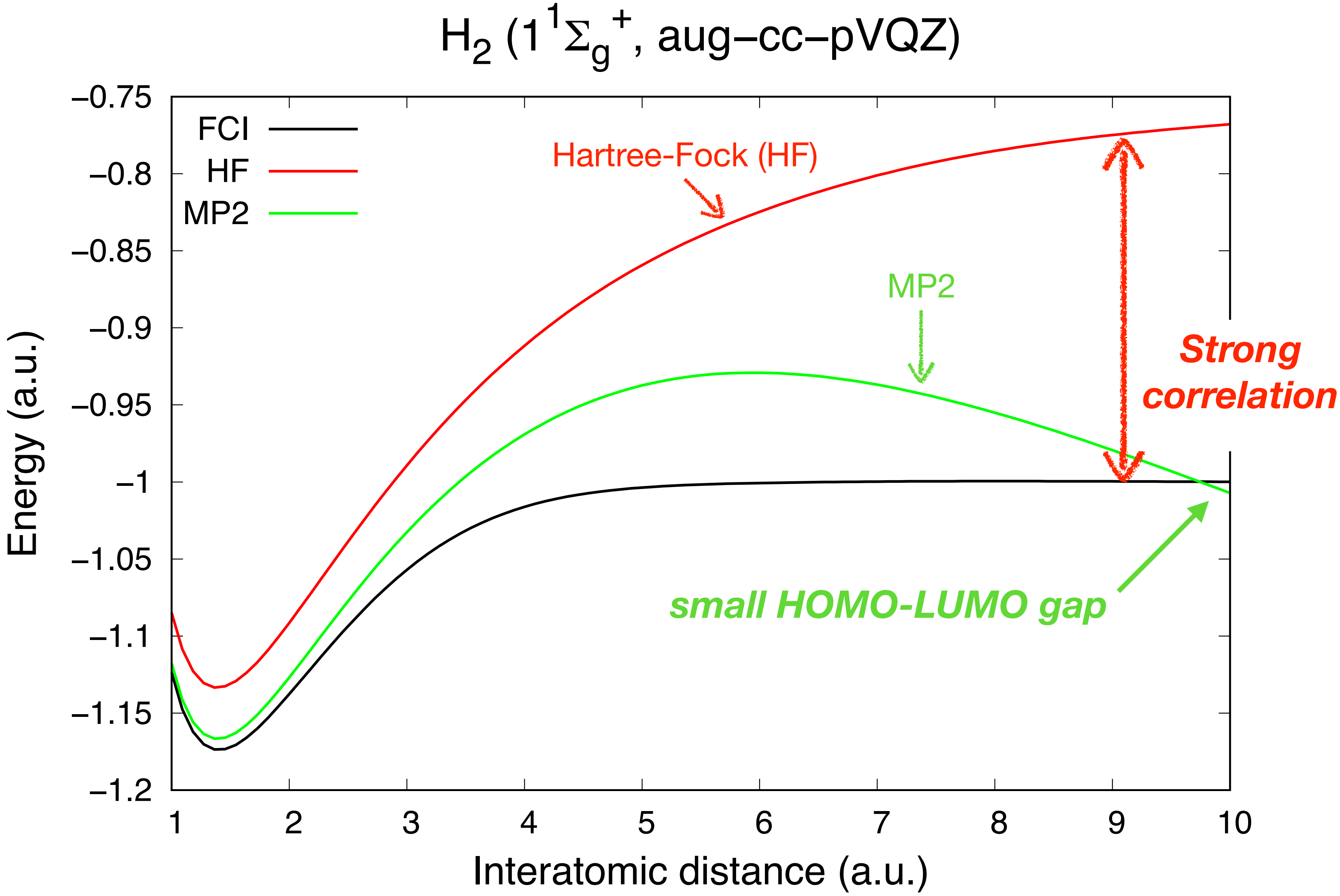


$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

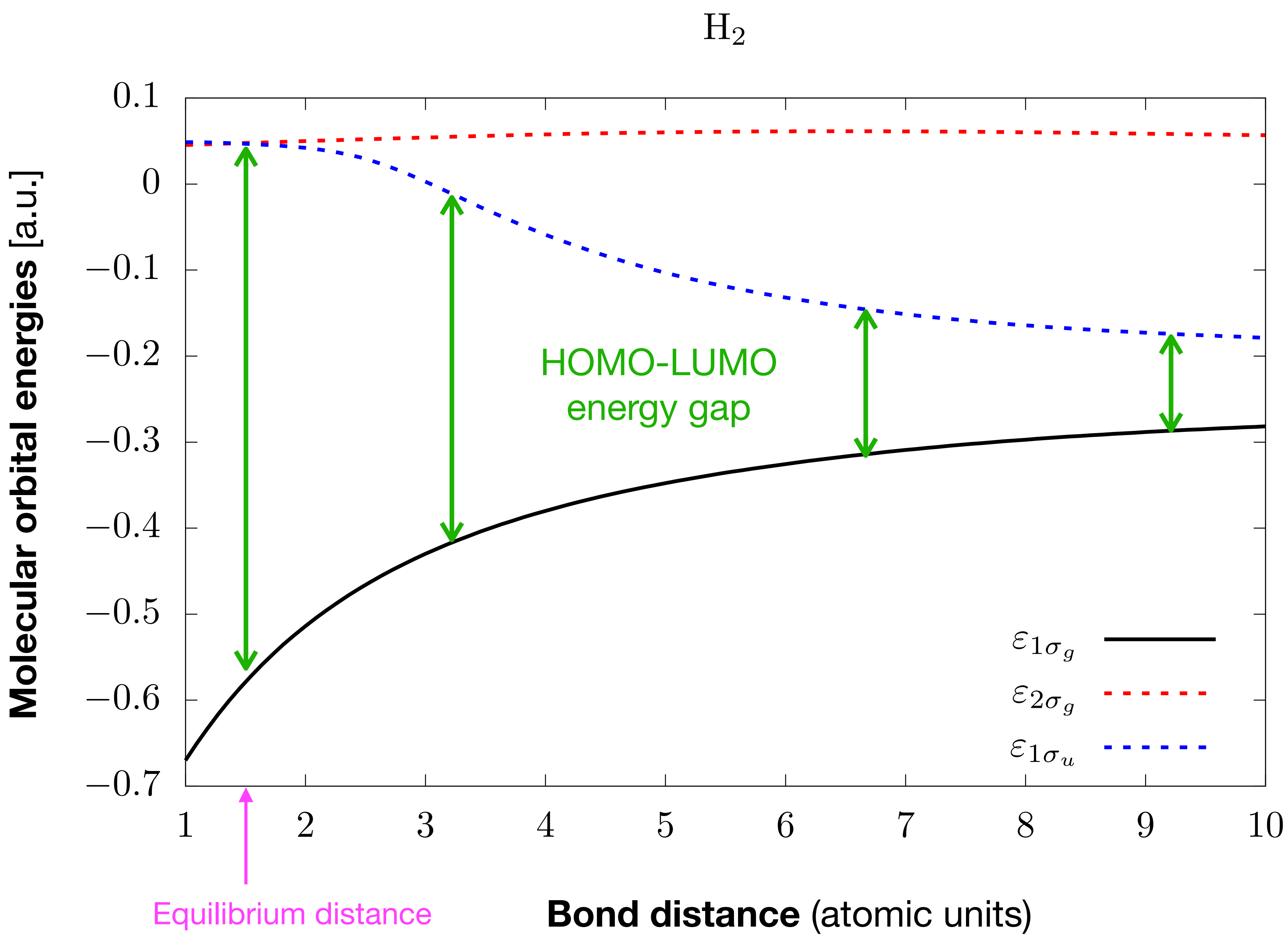
H^- ······ H^+ $\quad$ H^+ ······ H^-

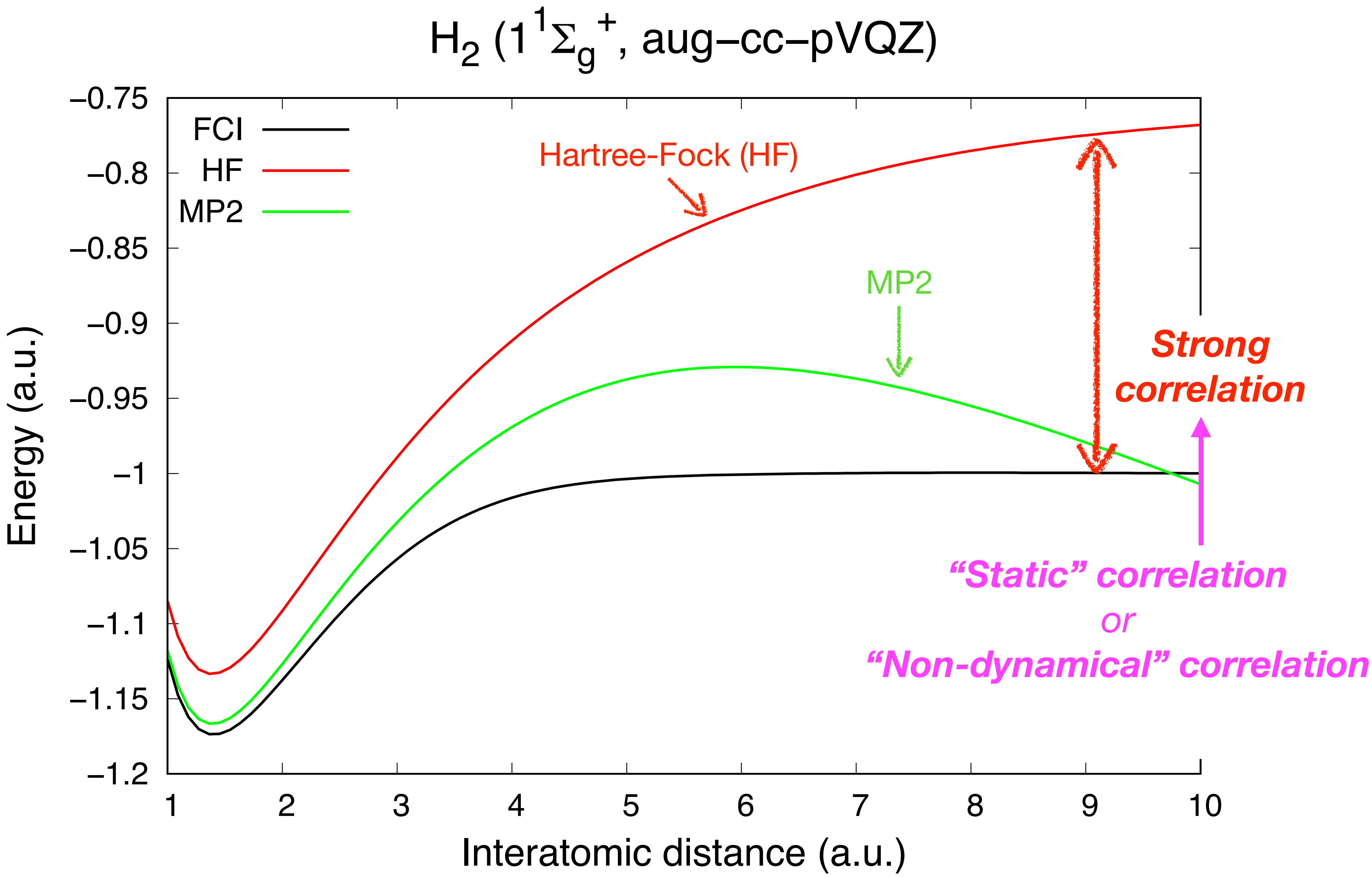


$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \boxed{\chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)}\right)$$


H2 (1 1Σg+, aug–cc–pVQZ)
FCI
HF
MP2
Hartree-Fock (HF)
MP2
Strong correlation
small HOMO-LUMO gap
Energy (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
Interatomic distance (a.u.)

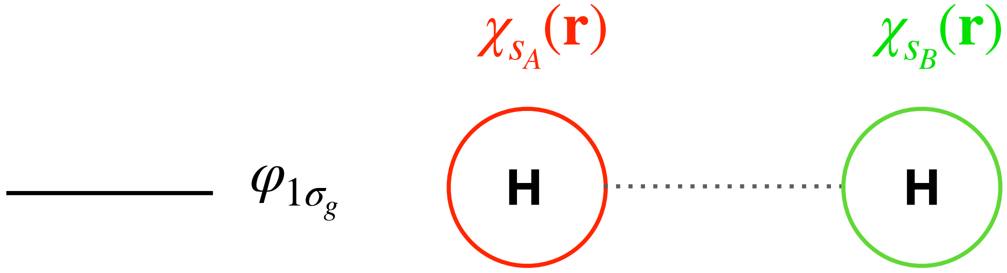
Near-degeneracy issues





H2 (1 1Σg+, aug–cc–pVQZ)
Energy (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
Interatomic distance (a.u.)
FCI
HF
MP2
Hartree-Fock (HF)
MP2
Strong correlation
"Static" correlation
or
"Non-dynamical" correlation

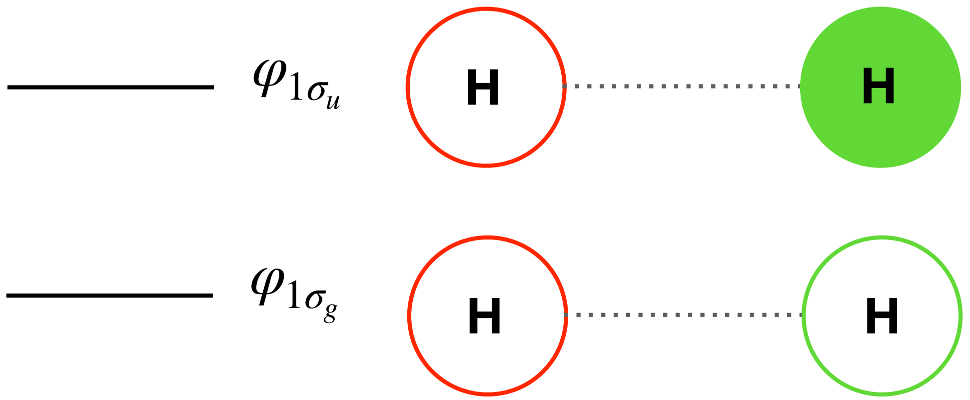
Multi-configurational wave function



Bonding orbital

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

Multi-configurational wave function



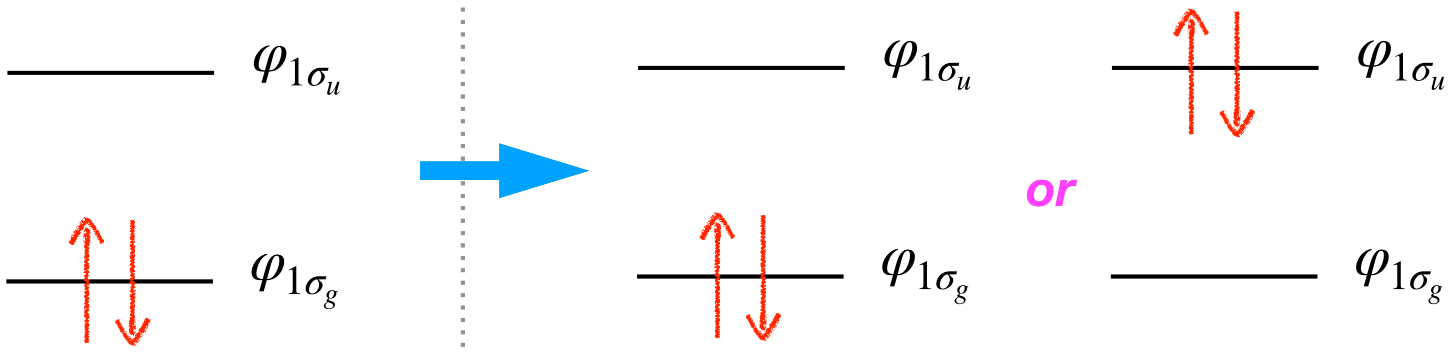
$\varphi_{1\sigma_u}$

$\varphi_{1\sigma_g}$

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

Anti-bonding orbital

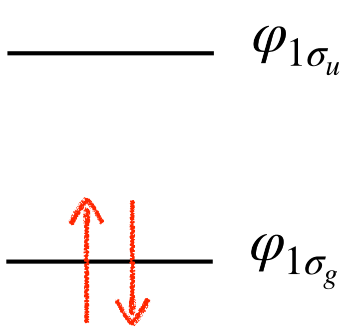
Multi-configurational wave function



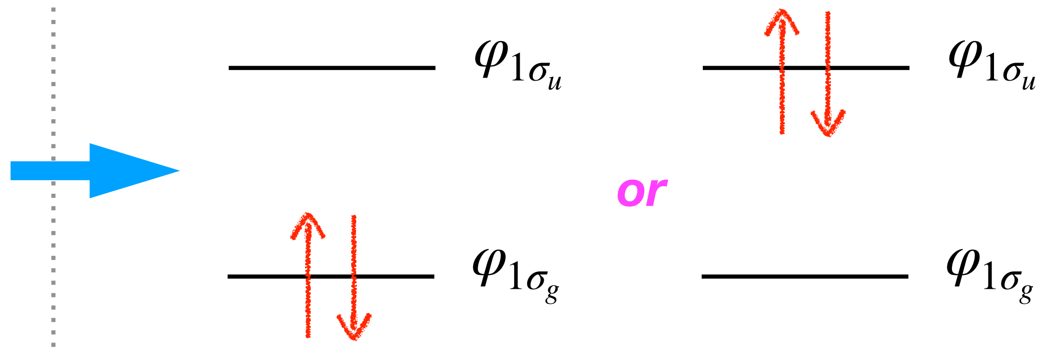
$$\left|\left(1\sigma_g\right)^2\right\rangle$$

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

Multi-configurational wave function



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



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

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

Multi-configurational wave function

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

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

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

Multi-configurational wave function

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

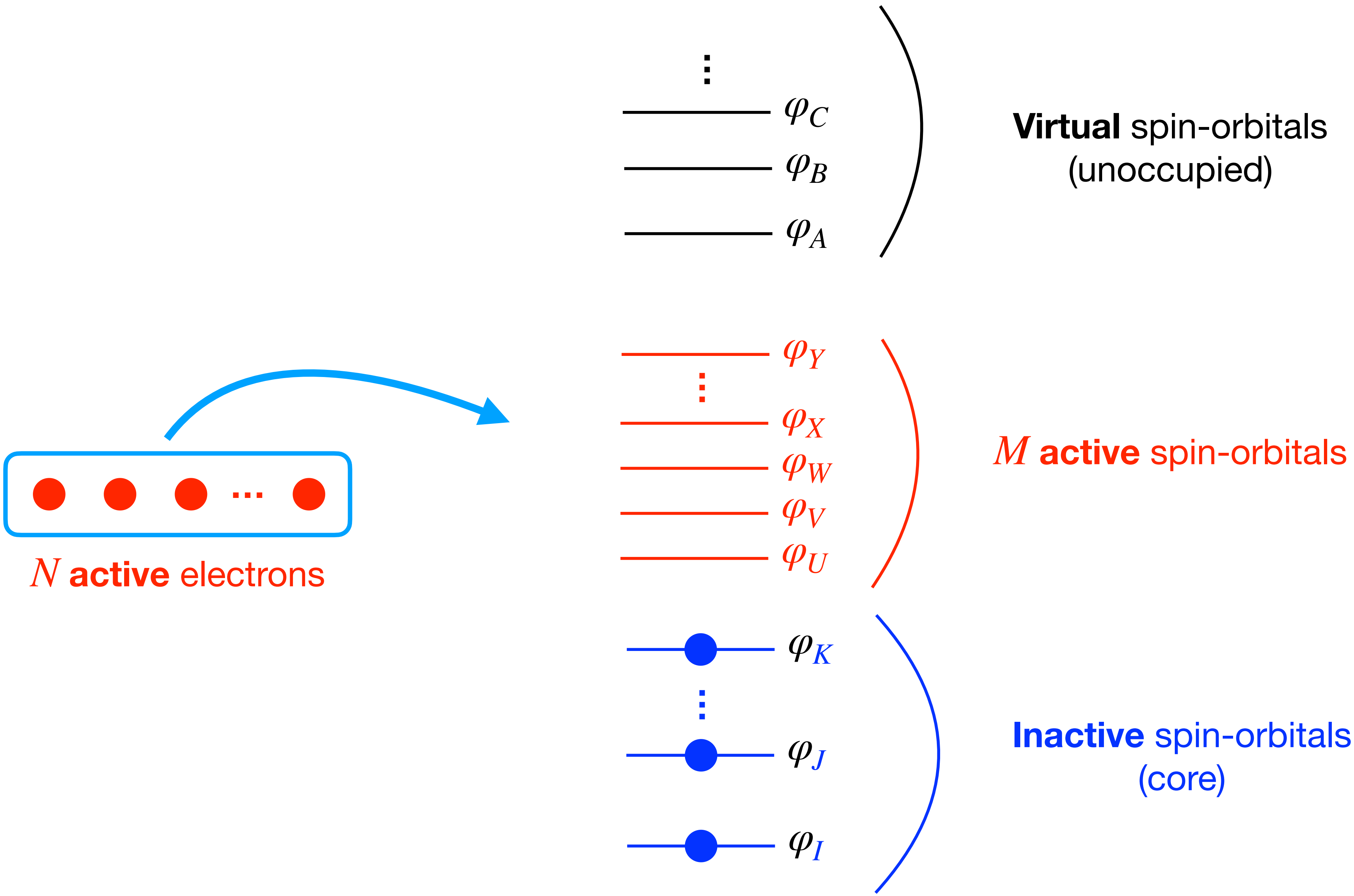
$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

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

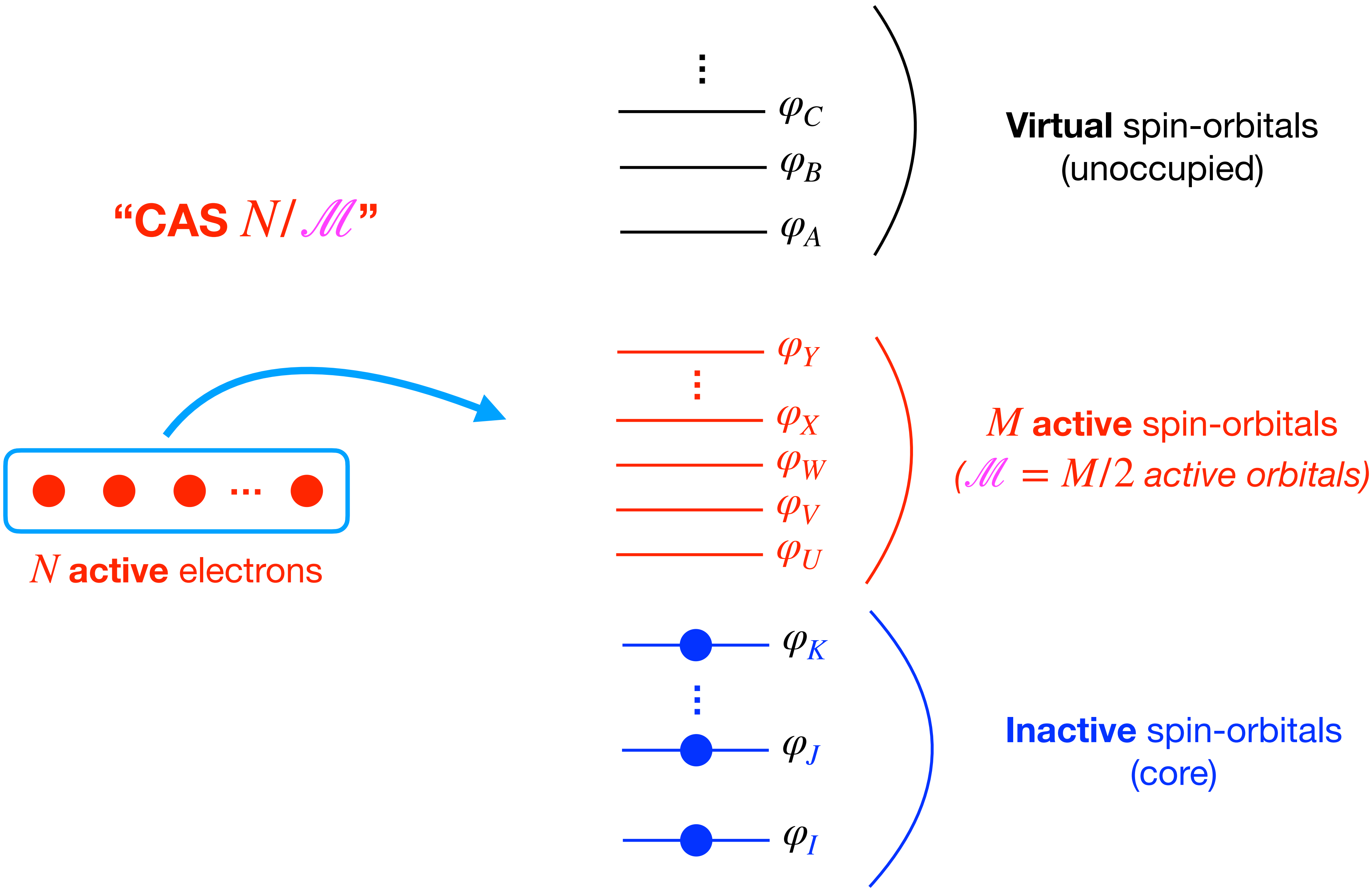
Multi-configurational wave function

$$\Psi \equiv \frac{1}{\sqrt{2}}\Big(\overbrace{\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)}^{\Phi_{(1\sigma_g)^2}} - \overbrace{\varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)}^{\Phi_{(1\sigma_u)^2}}\Big)$$

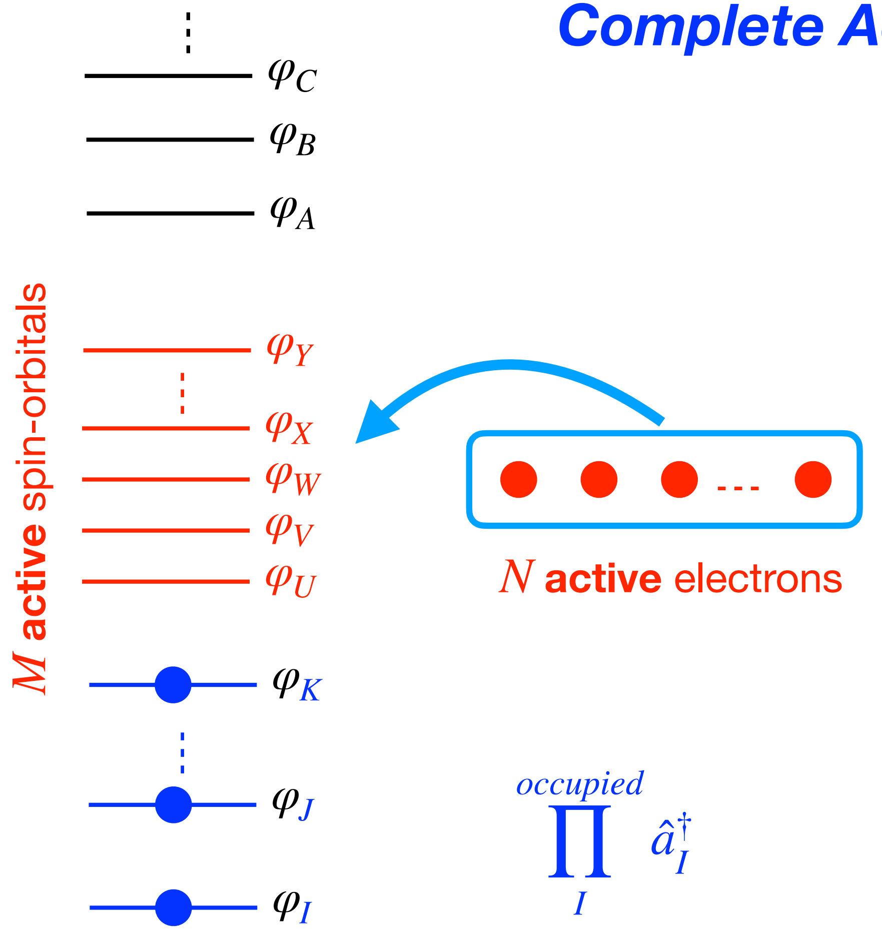
Complete Active Space CI (CASCI)



Complete Active Space CI (CASCI)



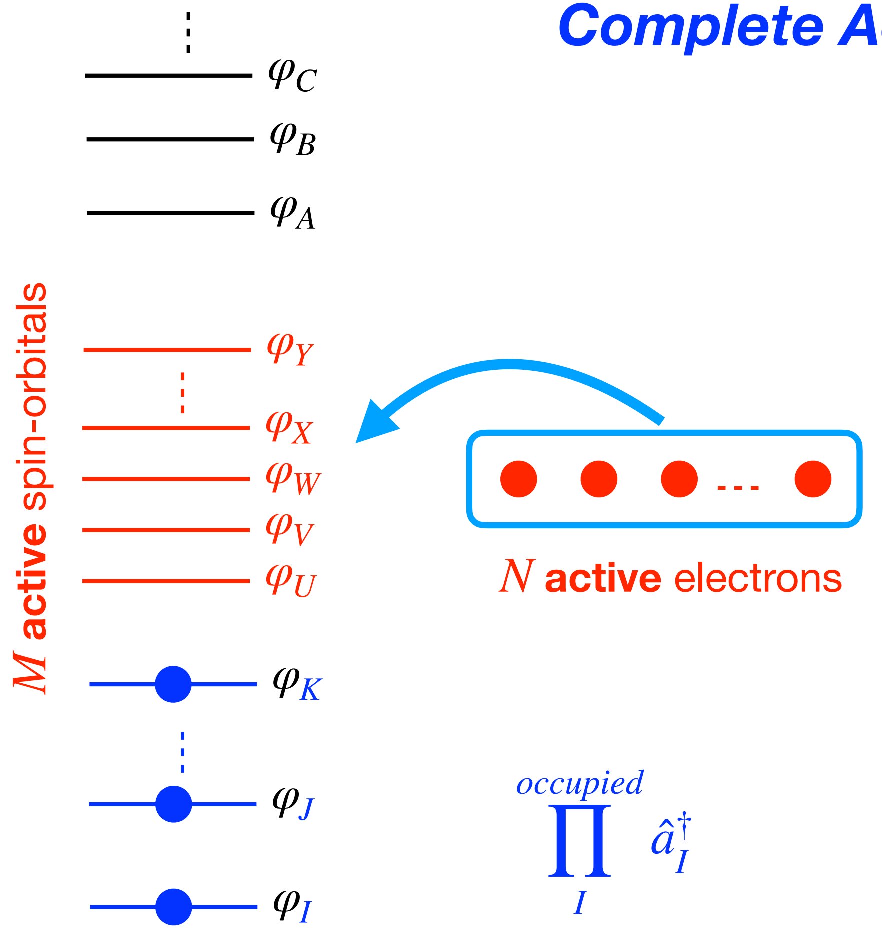
Complete Active Space CI (CASCI)



$$\prod_{I}^{occupied} \hat{a}_I^\dagger$$

$$|\Psi^{CASCI}\rangle = \hat{\Phi}^\dagger_{core} \sum_{(n_U,n_V,\ldots,n_Y)\in\{0,1\}^M}^{n_U+n_V+\ldots+n_Y=N} C_{n_U n_V \ldots n_Y} \left(\hat{a}_U^\dagger\right)^{n_U} \left(\hat{a}_V^\dagger\right)^{n_V} \ldots \left(\hat{a}_Y^\dagger\right)^{n_Y} |\,\text{vac}\rangle$$

Complete Active Space CI (CASCI)

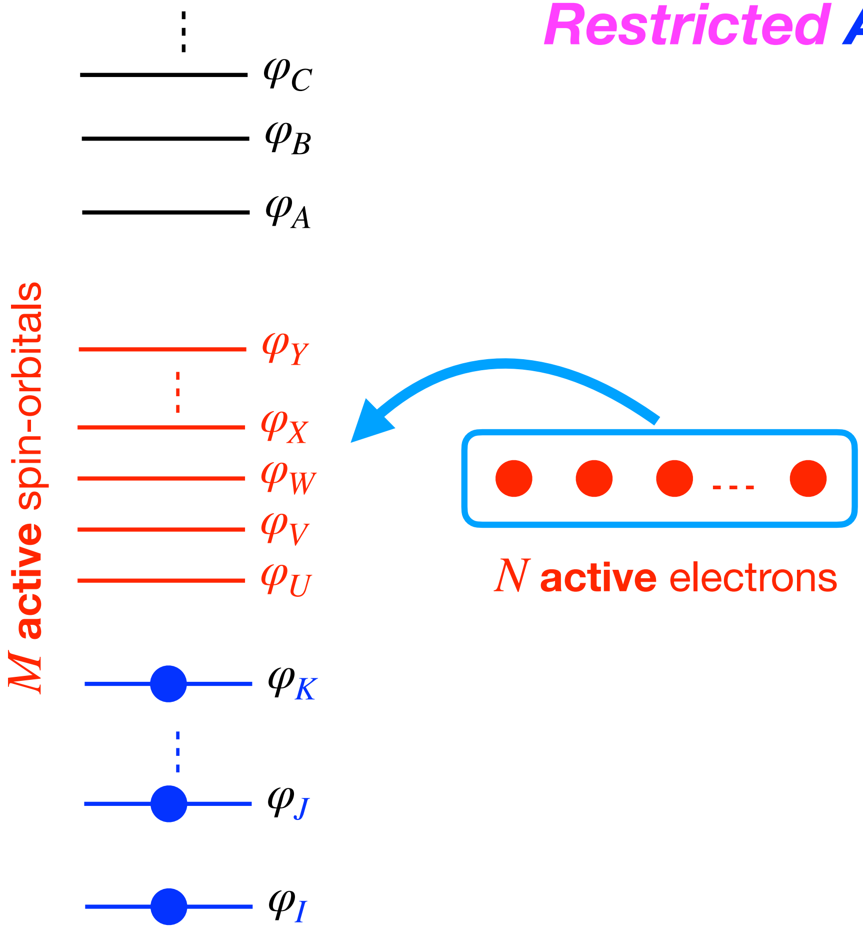


$$\prod_{I}^{occupied} \hat{a}_I^\dagger$$

FCI in the active orbital space!

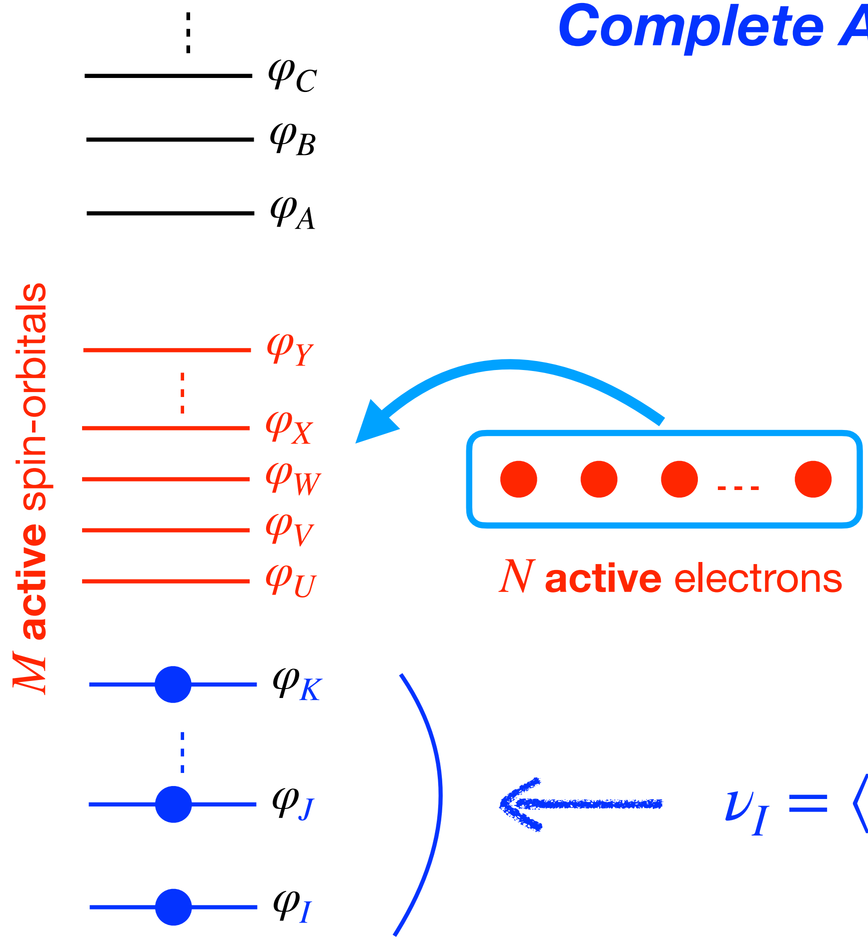
$$|\Psi^{CASCI}\rangle = \hat{\Phi}_{core}^\dagger \sum_{(n_U,n_V,\ldots,n_Y)\in\{0,1\}^M}^{n_U+n_V+\ldots+n_Y=N} C_{n_U n_V \ldots n_Y} \left(\hat{a}_U^\dagger\right)^{n_U} \left(\hat{a}_V^\dagger\right)^{n_V} \ldots \left(\hat{a}_Y^\dagger\right)^{n_Y} |\,\mathrm{vac}\rangle$$

Restricted *Active Space CI (RASCI)*



Truncated CI in the active orbital space!

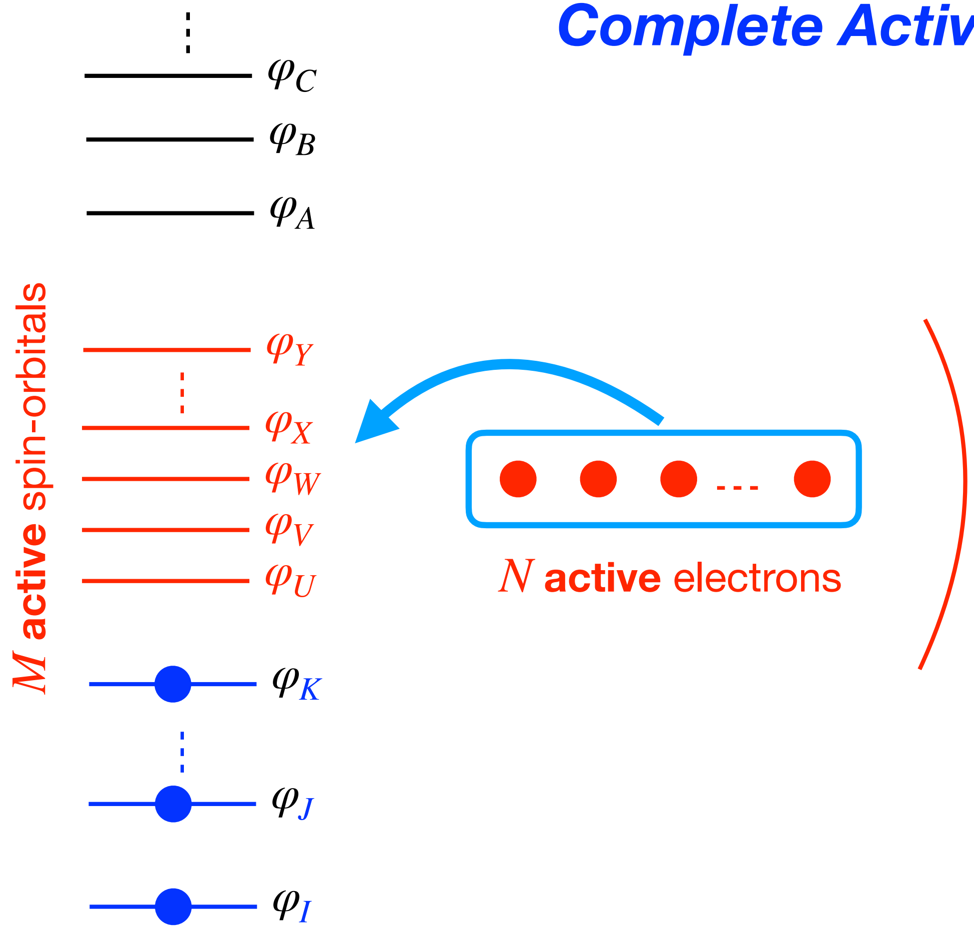
Complete Active Space CI (CASCI)



$$\nu_I = \langle \hat{a}_I^\dagger \hat{a}_I \rangle_{\Psi^{CASCI}} = \nu_J = \ldots = \nu_K = 1$$

$$|\Psi^{CASCI}\rangle = \hat{\Phi}^\dagger_{core} \sum_{(n_U, n_V, \ldots, n_Y) \in \{0,1\}^M}^{n_U + n_V + \ldots + n_Y = N} C_{n_U n_V \ldots n_Y} \left(\hat{a}_U^\dagger\right)^{n_U} \left(\hat{a}_V^\dagger\right)^{n_V} \ldots \left(\hat{a}_Y^\dagger\right)^{n_Y} |\mathrm{vac}\rangle$$

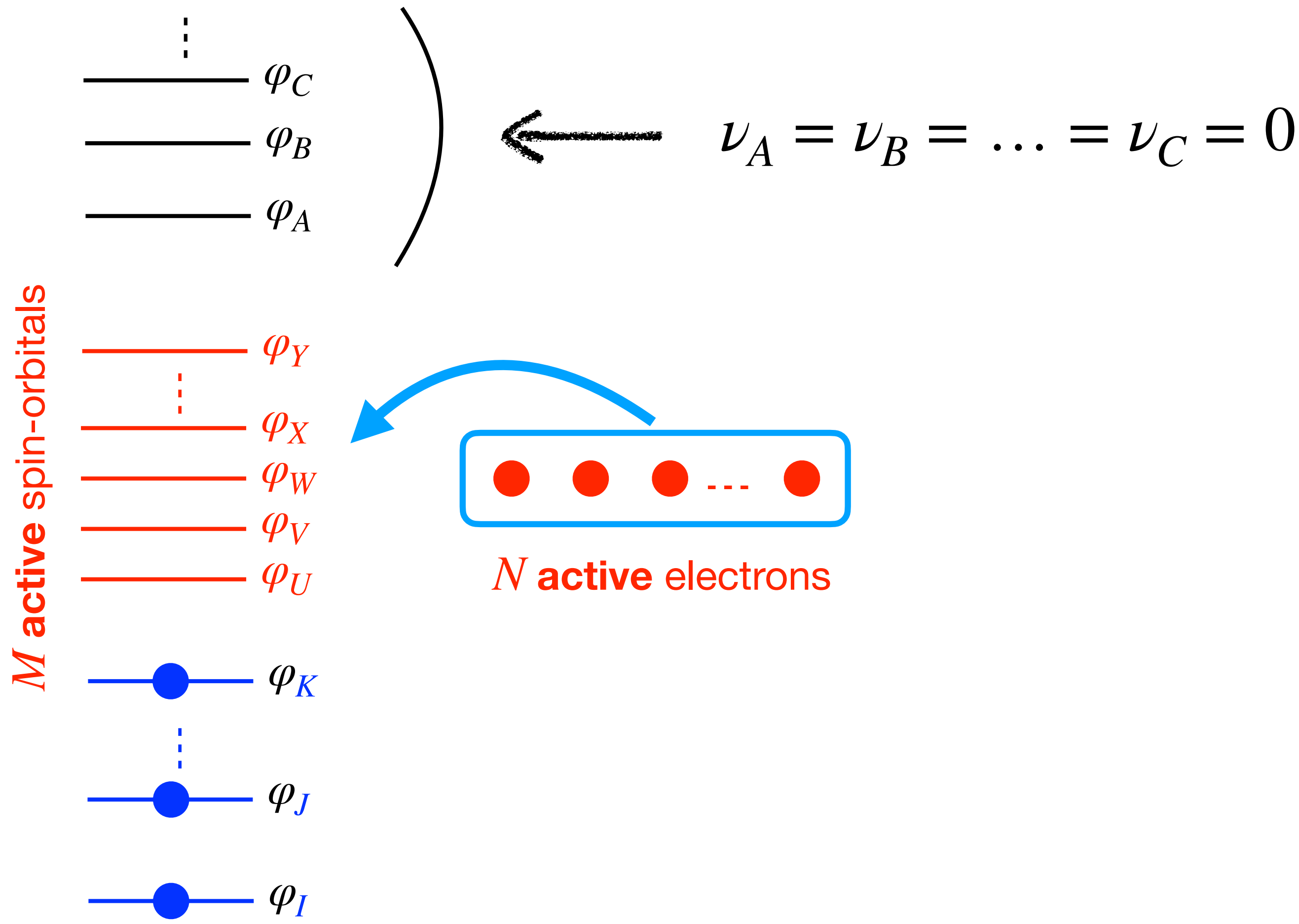
Complete Active Space CI (CASCI)



$$0 < \nu_U, \nu_V, \ldots, \nu_Y < 1$$

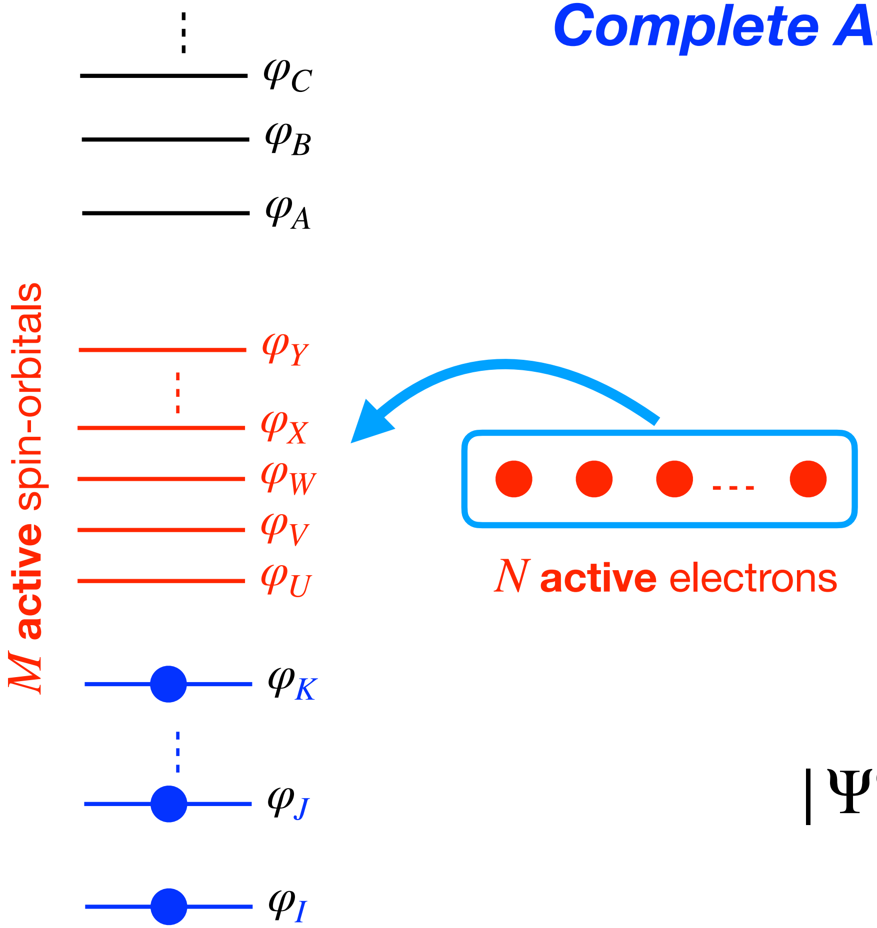
Fractional
occupation numbers!

$$|\Psi^{CASCI}\rangle = \hat{\Phi}^{\dagger}_{core} \sum_{(n_U,n_V,\ldots,n_Y)\in\{0,1\}^M}^{n_U+n_V+\ldots+n_Y=N} C_{n_U n_V \ldots n_Y} \left(\hat{a}^{\dagger}_U\right)^{n_U} \left(\hat{a}^{\dagger}_V\right)^{n_V} \ldots \left(\hat{a}^{\dagger}_Y\right)^{n_Y} |\,\mathrm{vac}\rangle$$



$$|\Psi^{CASCI}\rangle = \hat{\Phi}^{\dagger}_{core} \sum_{(n_U, n_V, \ldots, n_Y) \in \{0,1\}^M}^{n_U + n_V + \ldots + n_Y = N} C_{n_U n_V \ldots n_Y} \left(\hat{a}^{\dagger}_U\right)^{n_U} \left(\hat{a}^{\dagger}_V\right)^{n_V} \ldots \left(\hat{a}^{\dagger}_Y\right)^{n_Y} |\,\mathrm{vac}\rangle$$

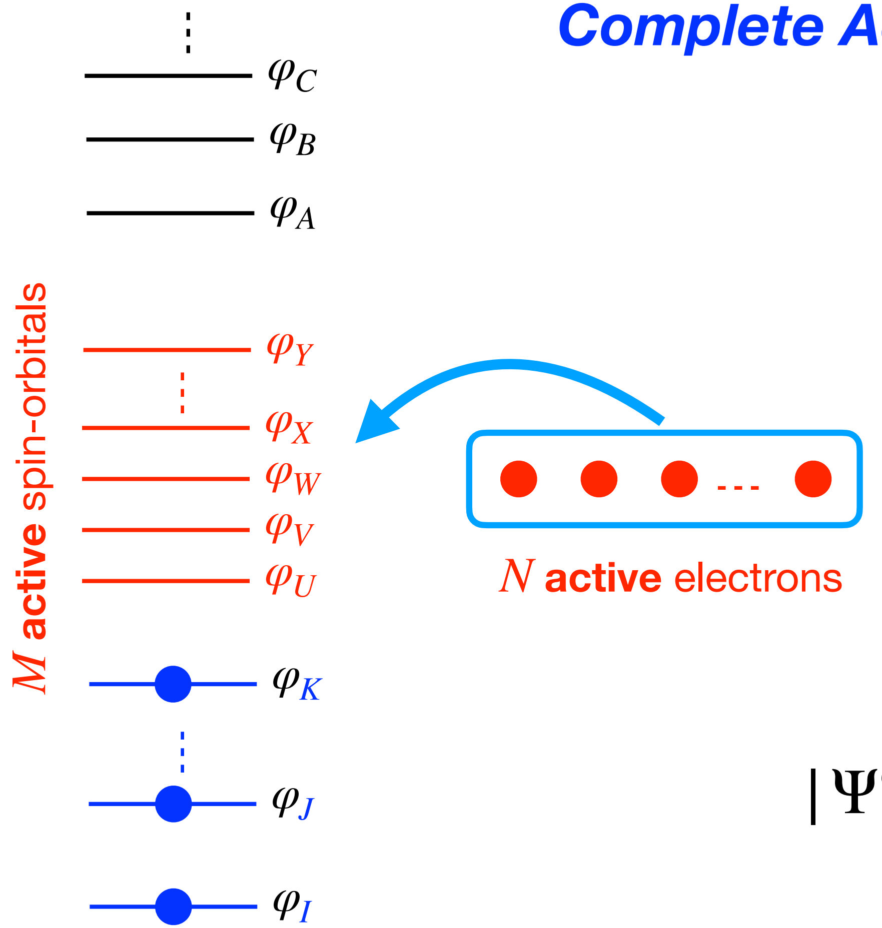
Complete Active Space CI (CASCI)



$$|\Psi^{CASCI}\rangle \overset{notation}{=} \sum_{\xi \in CAS} C_\xi |\Phi_\xi\rangle$$

$$|\Psi^{CASCI}\rangle = \hat{\Phi}^\dagger_{core} \sum_{(n_U, n_V, \ldots, n_Y) \in \{0,1\}^M}^{n_U + n_V + \ldots + n_Y = N} C_{n_U n_V \ldots n_Y} \left(\hat{a}^\dagger_U\right)^{n_U} \left(\hat{a}^\dagger_V\right)^{n_V} \ldots \left(\hat{a}^\dagger_Y\right)^{n_Y} |\mathrm{vac}\rangle$$

Complete Active Space CI (CASCI)



?????

$$|\Psi^{CASCI}\rangle \overset{notation}{=} \sum_{\xi\in CAS} C_{\xi} |\Phi_{\xi}\rangle$$

$$|\Psi^{CASCI}\rangle = \hat{\Phi}^{\dagger}_{core} \sum_{(n_U,n_V,\ldots,n_Y)\in\{0,1\}^M}^{n_U+n_V+\ldots+n_Y=N} C_{n_U n_V \ldots n_Y} \left(\hat{a}^{\dagger}_U\right)^{n_U} \left(\hat{a}^{\dagger}_V\right)^{n_V} \ldots \left(\hat{a}^{\dagger}_Y\right)^{n_Y} |\mathrm{vac}\rangle$$

Diagonalization of the CASCI Hamiltonian matrix

$$\left\{ \langle \Phi_\xi | \hat{H} | \Phi_{\xi'} \rangle \right\}_{(\xi,\xi')\in CAS^2}$$

$$\uparrow$$

$$\mathbf{H}\mathbf{C} = E_n^{CASCI}\mathbf{C}$$

$$\downarrow$$

$$\left\{ C_\xi \right\}_{\xi\in CAS}$$

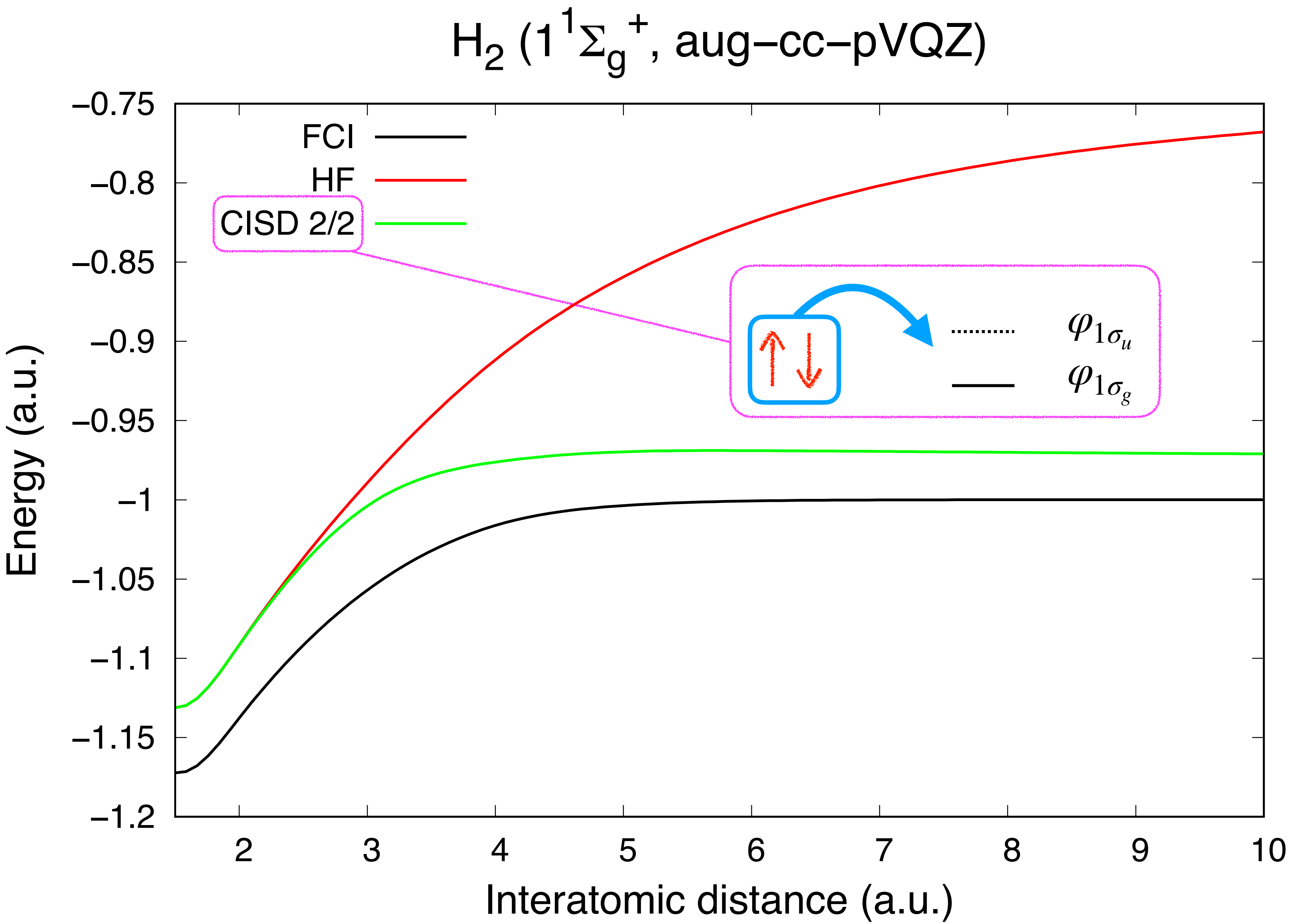
Diagonalization of the CASCI Hamiltonian matrix

$$\mathbf{H}\mathbf{C} = E_n^{CASCI}\mathbf{C}$$

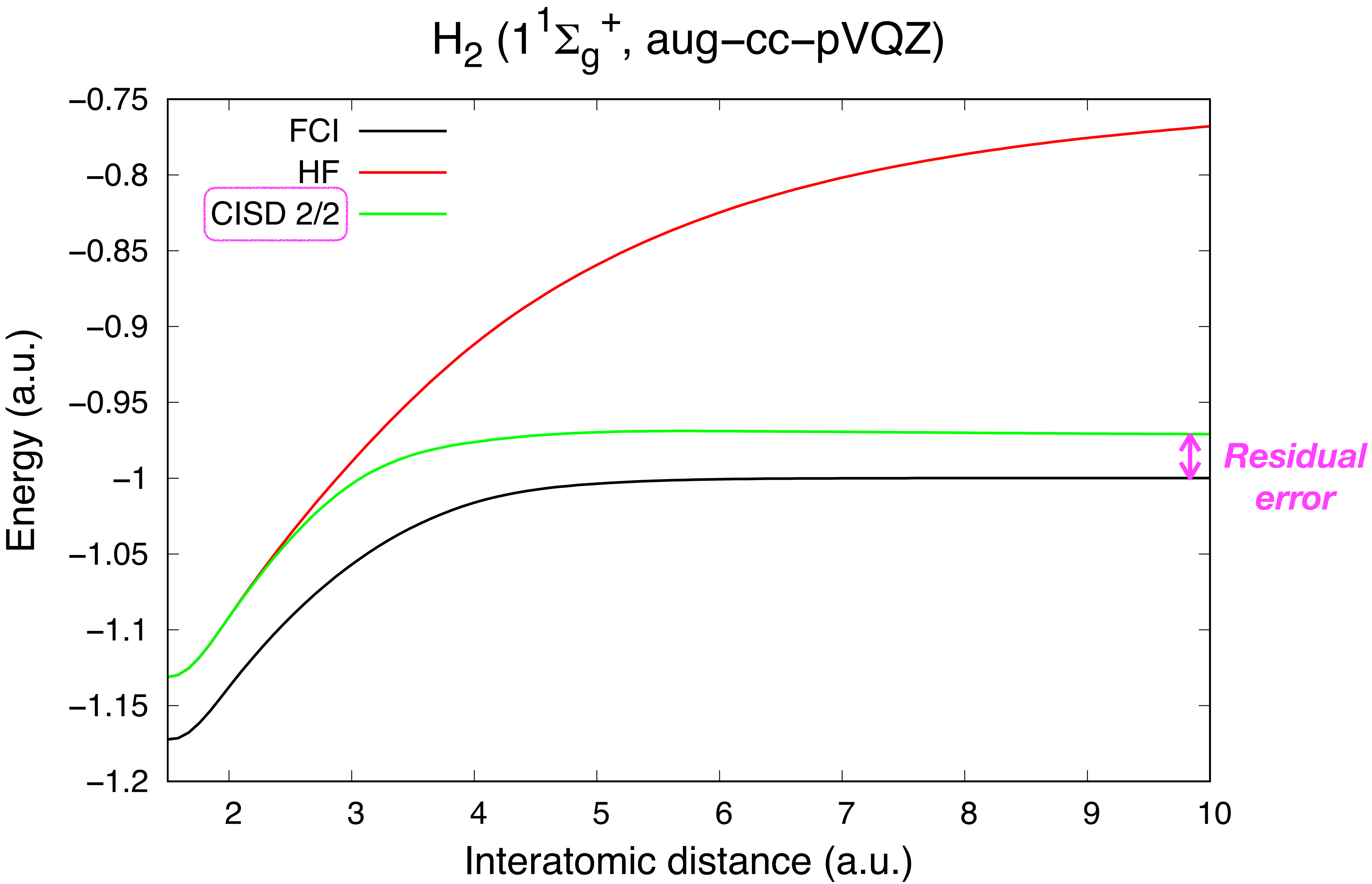
↓

Ground- ($n = 0$) or excited- ($n > 0$) state **energy**

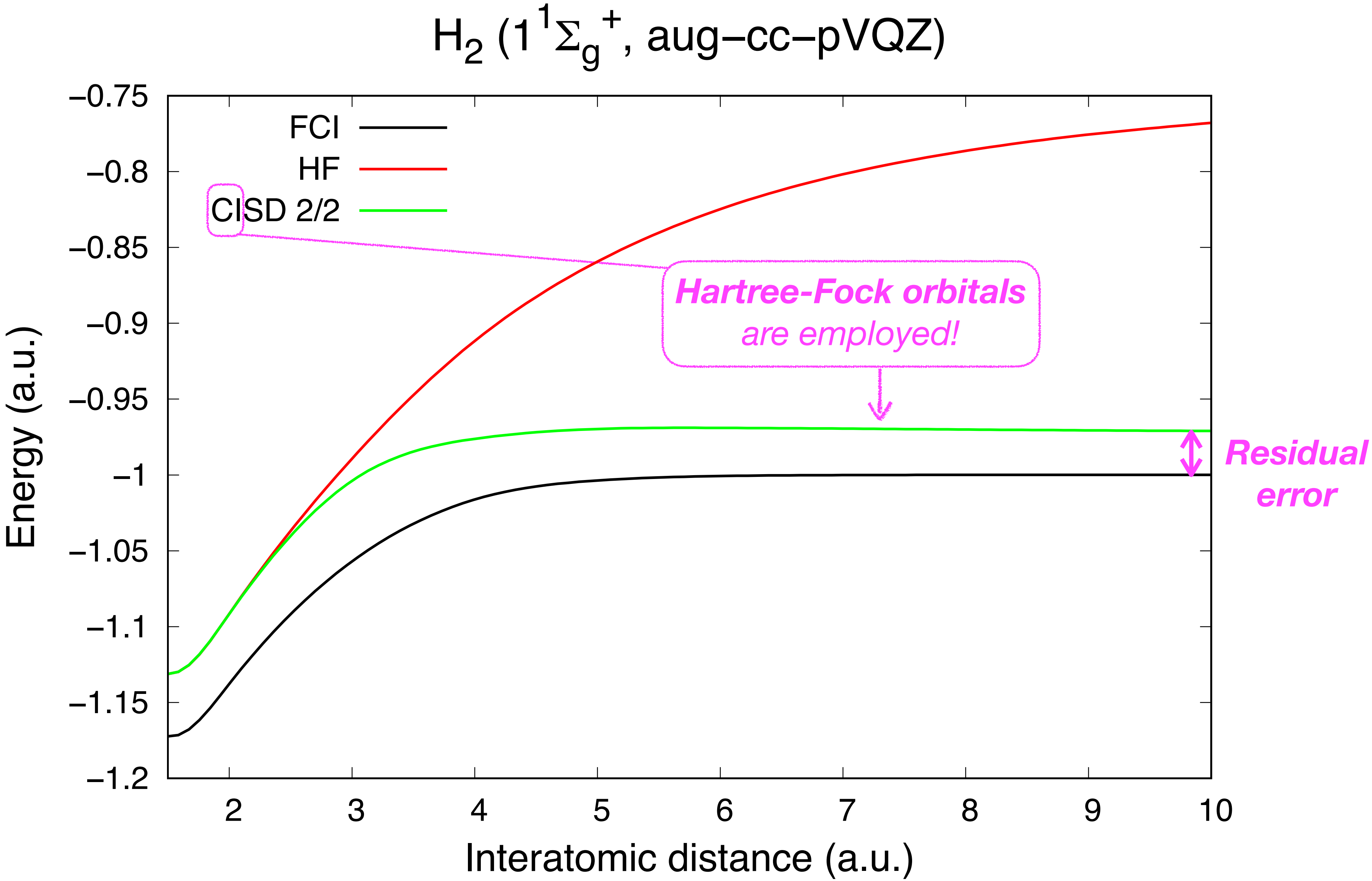
Dissociation of the hydrogen molecule



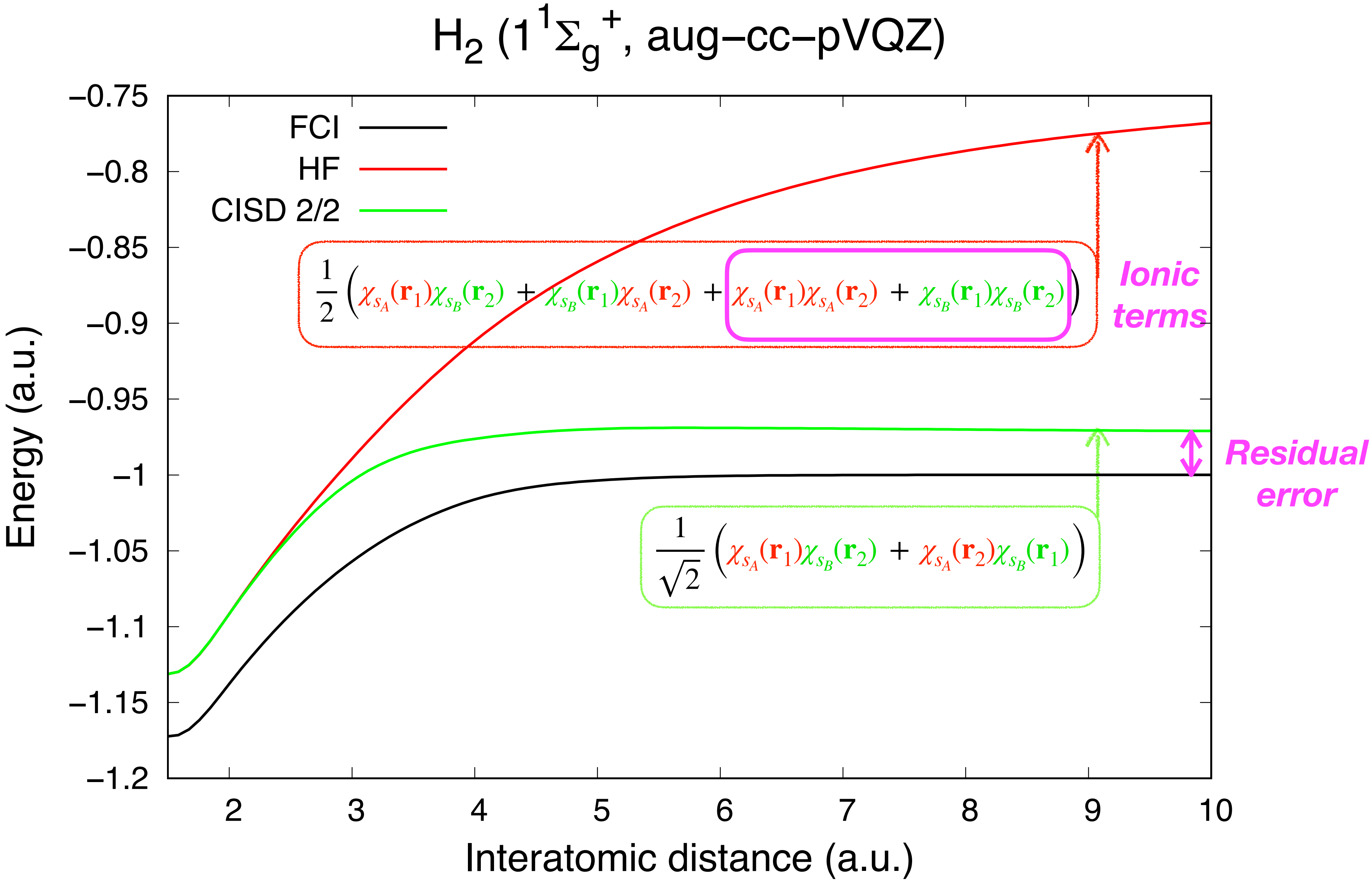
Dissociation of the hydrogen molecule



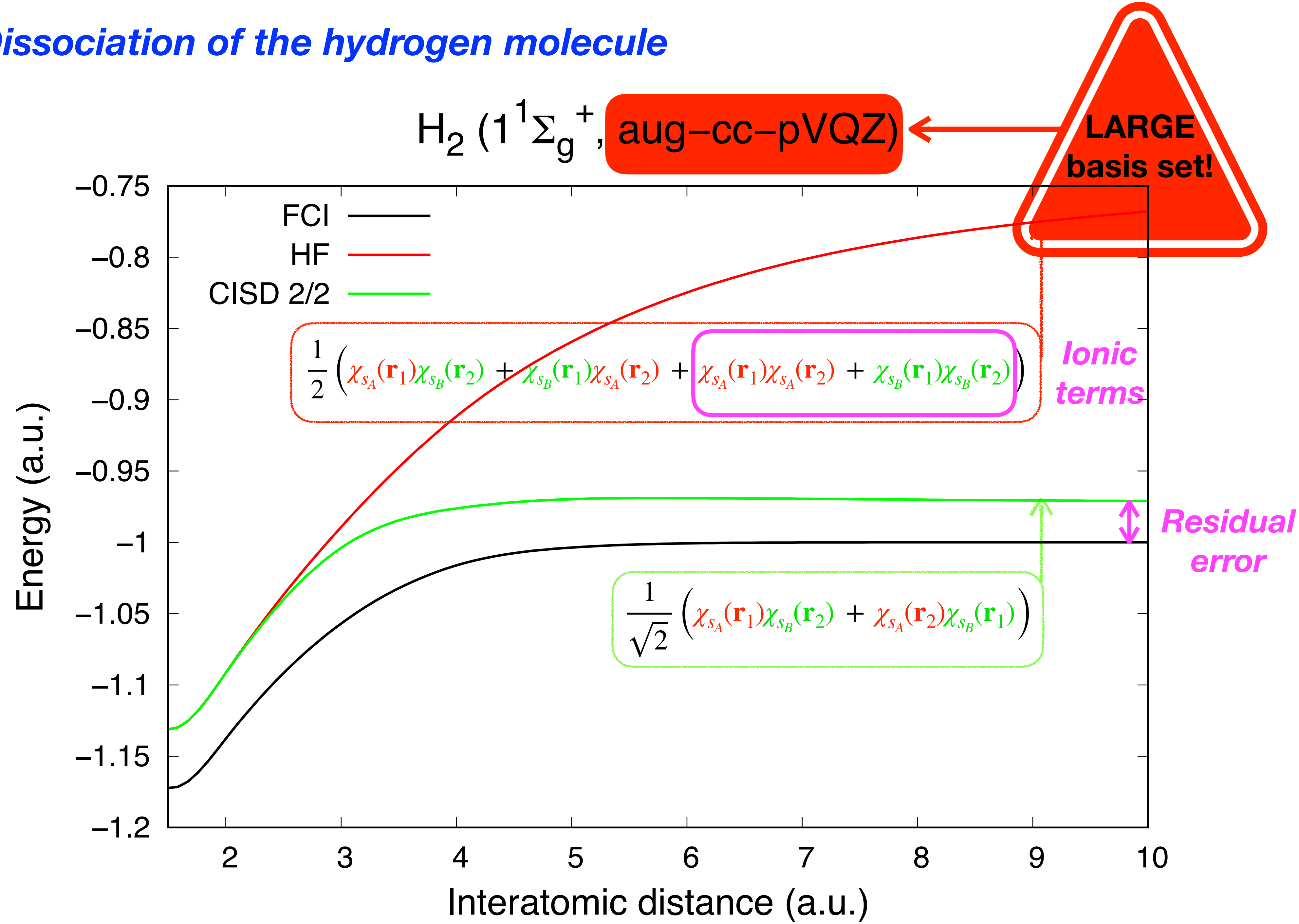
Dissociation of the hydrogen molecule



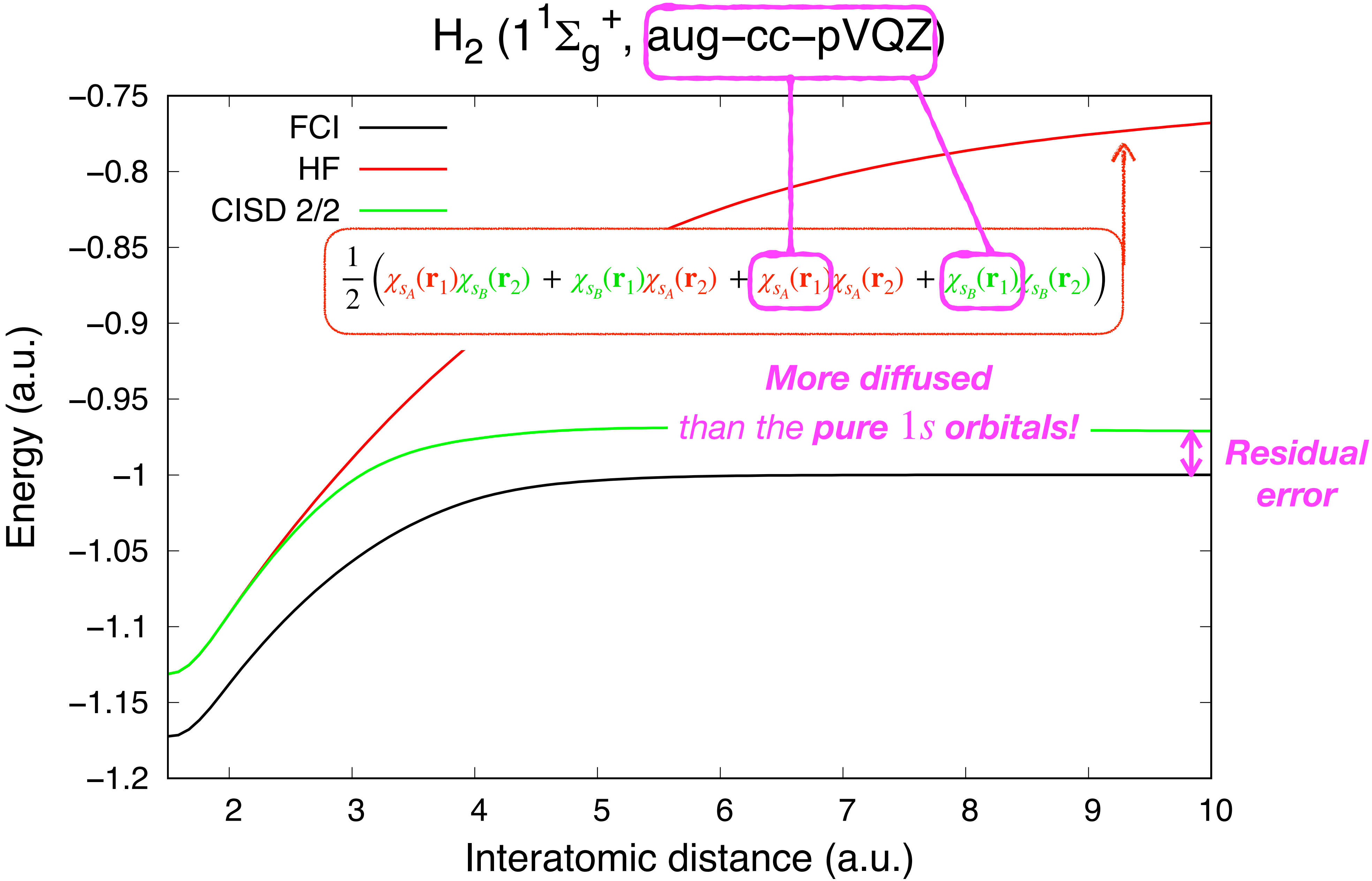
Dissociation of the hydrogen molecule



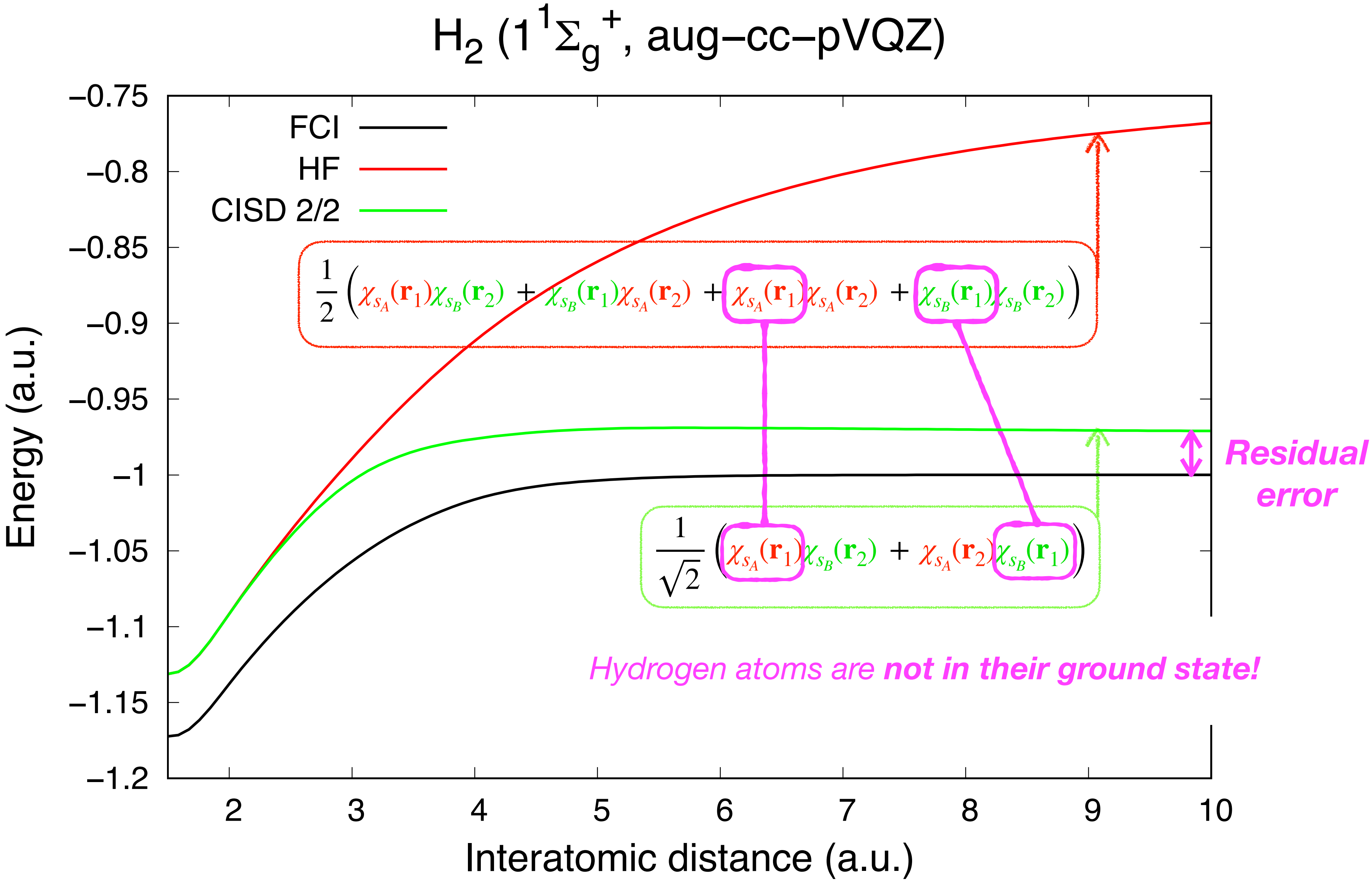
Dissociation of the hydrogen molecule



Dissociation of the hydrogen molecule



Dissociation of the hydrogen molecule



Important conclusion

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

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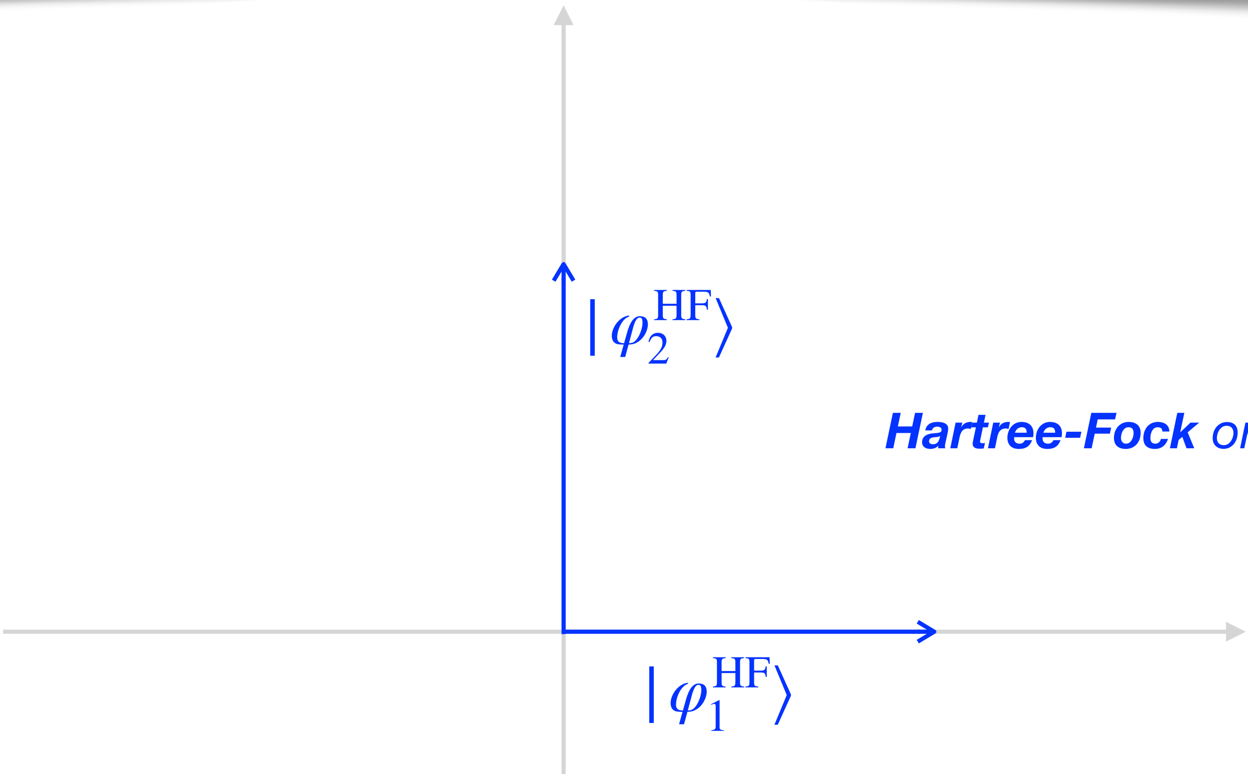
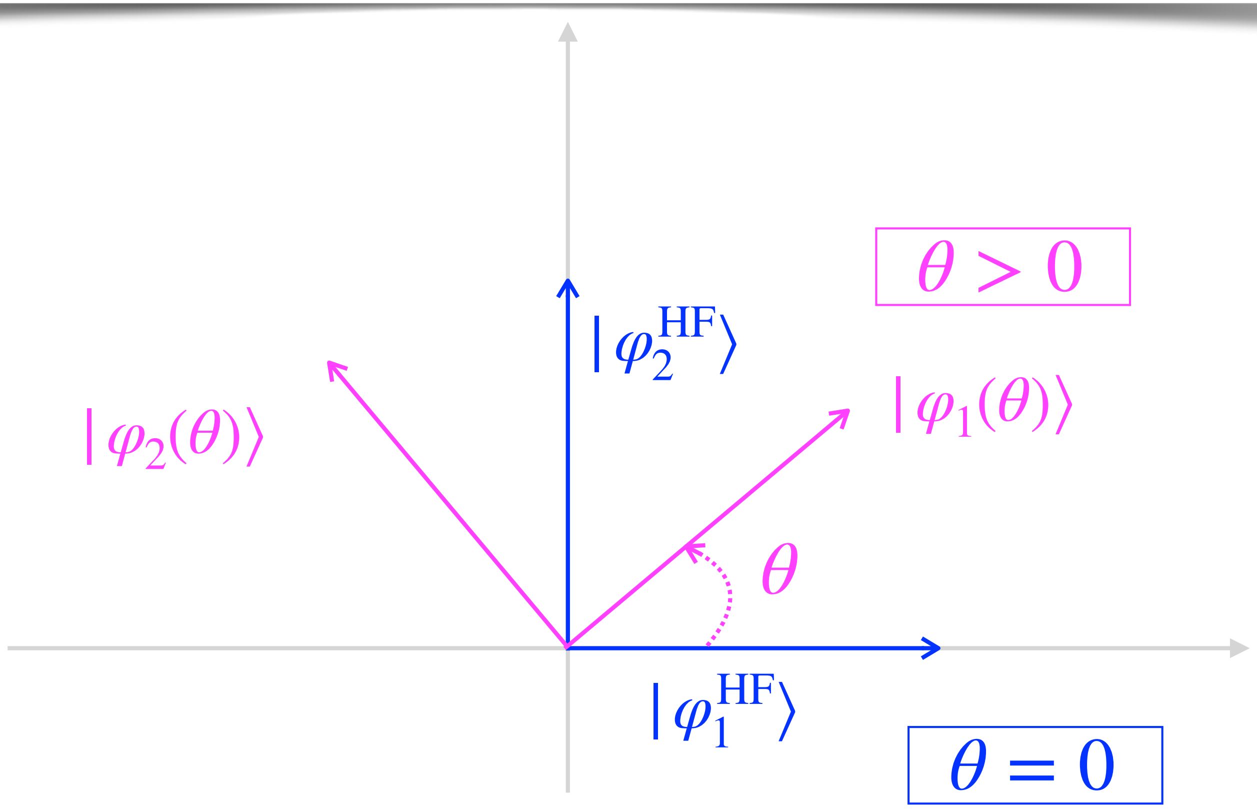
↓

Multi-Configurational Self-Consistent Field (MCSCF) approach

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

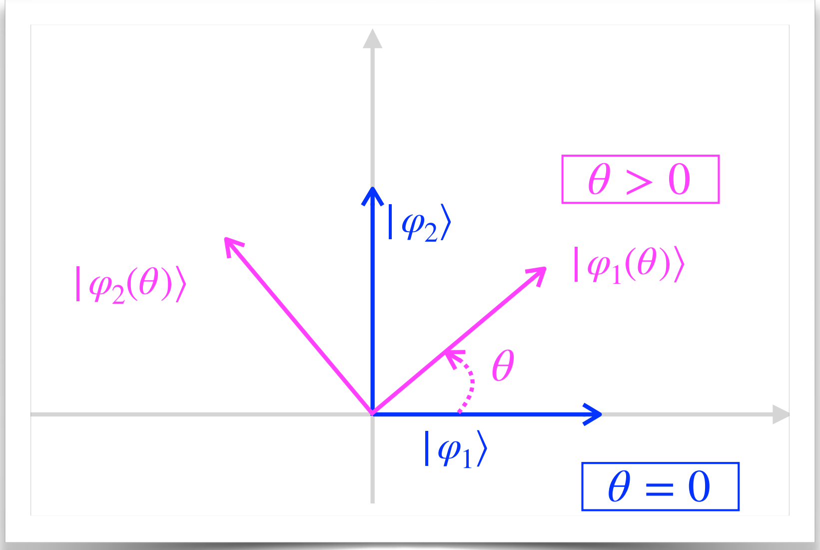


Multi-configurational *wave functions need a* ***re-optimization of the orbitals***



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

Orbital rotation

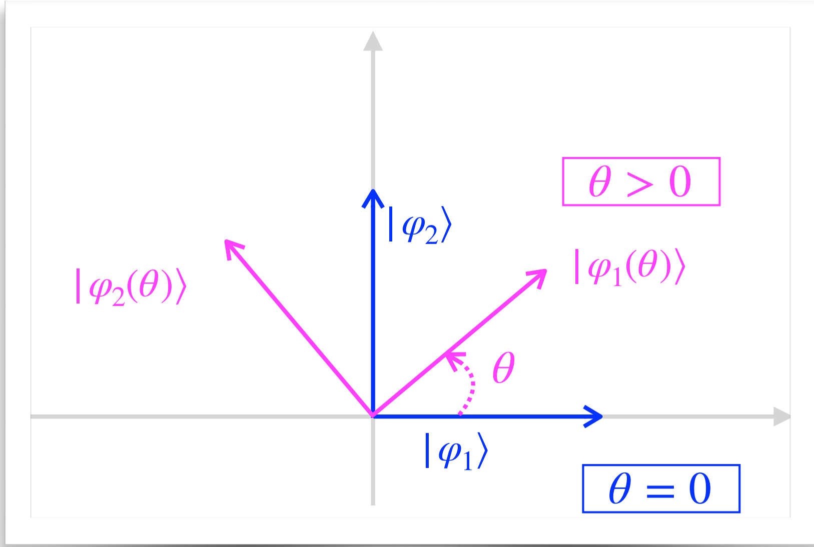


Multi-configurational *wave functions need a* ***re-optimization of the orbitals***

Orbital rotation

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

Matrix representation of the rotation



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

Orbital rotation

$$\begin{matrix} & |\varphi_1(\theta)\rangle & |\varphi_2(\theta)\rangle \\ \langle\varphi_1| & \cos\theta & -\sin\theta \\ \langle\varphi_2| & \sin\theta & \cos\theta \end{matrix}$$

$$\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} = \mathscr{U}(\theta) = e^{-\begin{bmatrix} 0 & \theta \\ -\theta & 0 \end{bmatrix}}$$

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

Orbital rotation

$$\begin{matrix} & |\varphi_1(\theta)\rangle & |\varphi_2(\theta)\rangle \\ \langle\varphi_1| & \cos\theta & -\sin\theta \\ \langle\varphi_2| & \sin\theta & \cos\theta \end{matrix}$$

$$\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} = e^{-\begin{bmatrix} 0 & \theta \\ -\theta & 0 \end{bmatrix}}$$

anti-hermitian!

$$\kappa(\theta) = -\kappa^{\dagger}(\theta)$$

Spin-orbital rotation in second quantization

"Unrotated" determinant $$|\Phi_\xi\rangle \equiv \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

Spin-orbital rotation in second quantization

"Unrotated" determinant

$$|\Phi_{\xi}\rangle \equiv \hat{a}^{\dagger}_{P_1}\hat{a}^{\dagger}_{P_2}\ldots\hat{a}^{\dagger}_{P_N}|\text{vac}\rangle$$

"Rotated" determinant

$$|\Phi_{\xi}(\kappa)\rangle \equiv \hat{a}^{\dagger}_{P_1(\kappa)}\hat{a}^{\dagger}_{P_2(\kappa)}\ldots\hat{a}^{\dagger}_{P_N(\kappa)}|\text{vac}\rangle$$

Spin-orbital rotation in second quantization

"Unrotated" determinant $$|\Phi_\xi\rangle \equiv \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_N}|\text{vac}\rangle$$

"Rotated" determinant $$|\Phi_\xi(\kappa)\rangle \equiv \hat{a}^\dagger_{P_1(\kappa)}\hat{a}^\dagger_{P_2(\kappa)}\ldots\hat{a}^\dagger_{P_N(\kappa)}|\text{vac}\rangle$$

$$= e^{-\hat{\kappa}}|\Phi_\xi\rangle$$

↑

***Same** operator*
***for all** the determinants!* 😀

Spin-orbital rotation in second quantization

"Unrotated" determinant

$$|\Phi_\xi\rangle \equiv \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\dots\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

"Rotated" determinant

$$|\Phi_\xi(\kappa)\rangle \equiv \hat{a}^\dagger_{P_1(\kappa)}\hat{a}^\dagger_{P_2(\kappa)}\dots\hat{a}^\dagger_{P_N(\kappa)}|\mathrm{vac}\rangle$$

$$= e^{-\hat{\kappa}}|\Phi_\xi\rangle$$

If we use real algebra…

$$\hat{\kappa} = \sum_{P<Q} \kappa_{PQ}\left(\hat{a}^\dagger_P\hat{a}_Q - \hat{a}^\dagger_Q\hat{a}_P\right) = -\hat{\kappa}^\dagger$$

Optimisation of the ground-state CASSCF wave function

$$|\Psi^{CASSCF}\rangle = e^{-\hat{\kappa}} \sum_{\xi \in CAS} C_\xi |\Phi_\xi\rangle = |\Psi(\lambda)\rangle$$

$$\lambda \equiv \left\{ \left\{ \kappa_{PQ} \right\}_{P<Q}, \left\{ C_\xi \right\}_{\xi \in CAS} \right\}$$

Variational parameters

Optimisation of the ground-state CASSCF wave function

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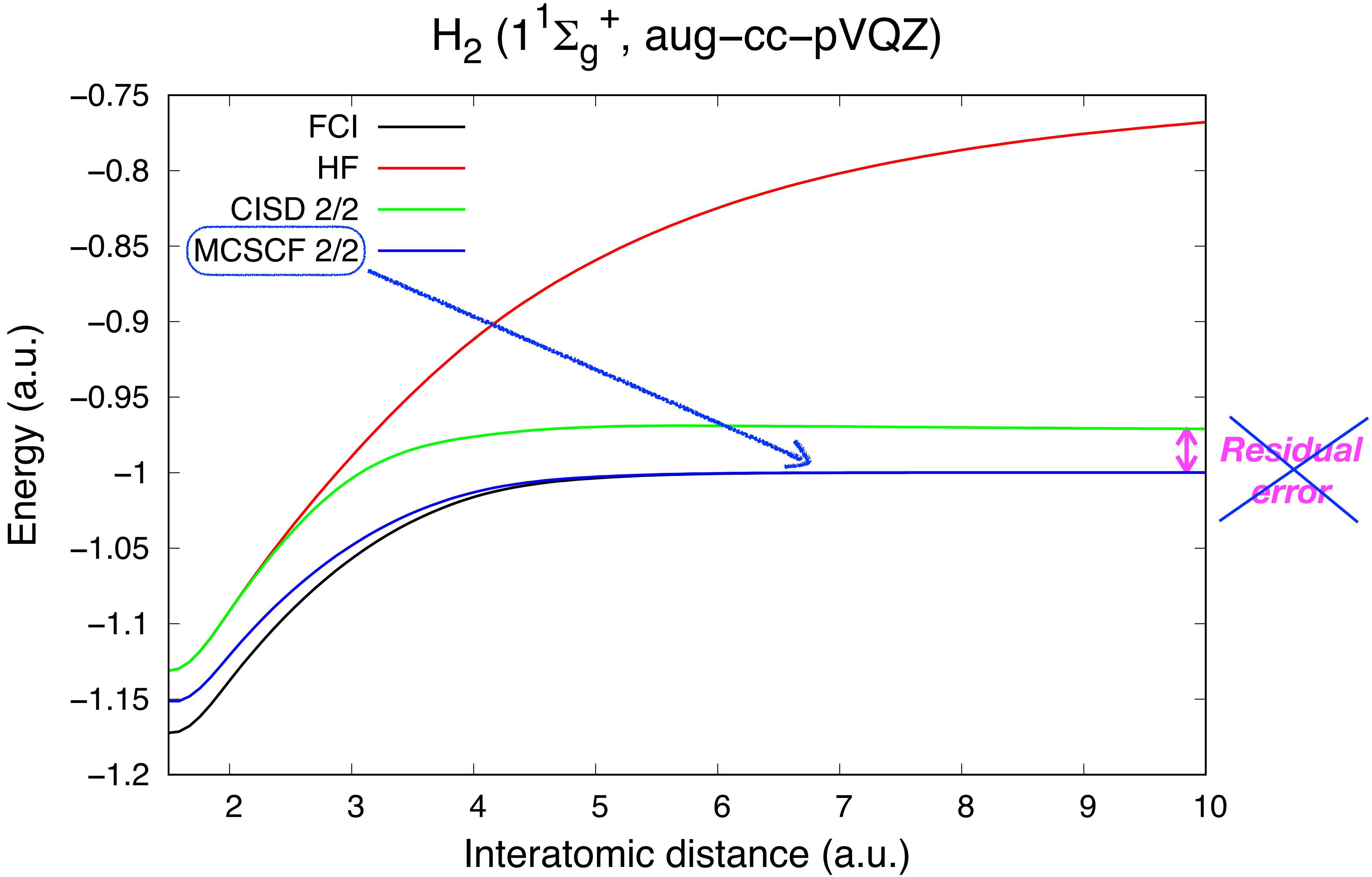
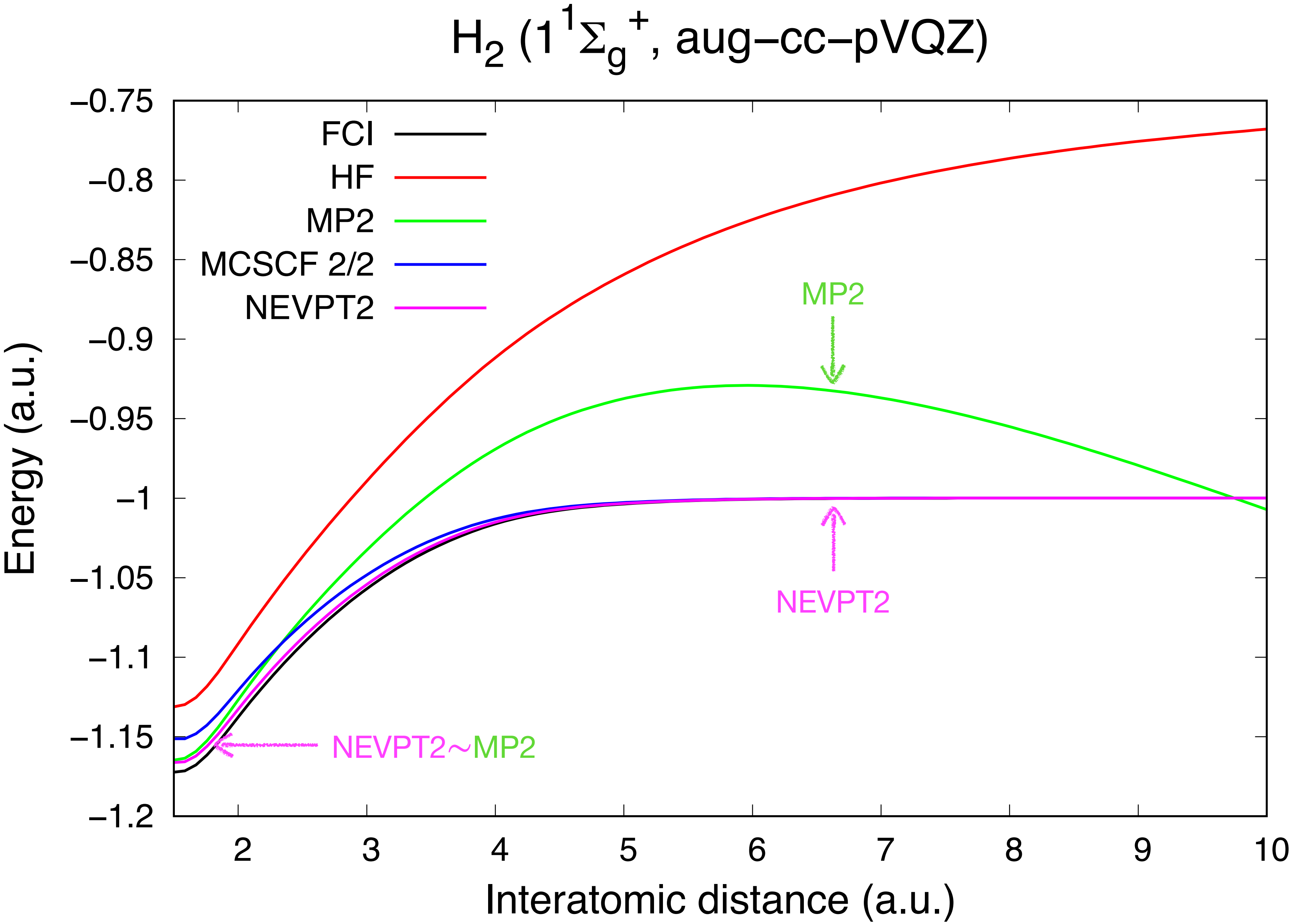
$$\lambda \equiv \left\{ \left\{ \kappa_{PQ} \right\}_{P<Q}, \left\{ C_\xi \right\}_{\xi \in CAS} \right\}$$

$$E_0^{CASSCF} = \min_{\lambda} \langle \Psi(\lambda) | \hat{H} | \Psi(\lambda) \rangle$$

Dissociation of the hydrogen molecule



Dissociation of the hydrogen molecule



Spin-orbital rotation in the vicinity of the minimizing CASSCF wave function

$$|\Psi(\kappa)\rangle = e^{-\hat{\kappa}}|\Psi_0^{CASSCF}\rangle$$

Spin-orbital rotation in the vicinity of the minimizing CASSCF wave function

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$$E_0^{CASSCF} = \min_{\kappa}\langle\Psi(\kappa)|\hat{H}|\Psi(\kappa)\rangle \overset{\kappa=0}{=} \langle\Psi_0^{CASSCF}|\hat{H}|\Psi_0^{CASSCF}\rangle$$

Spin-orbital rotation in the vicinity of the minimizing CASSCF wave function

$$|\Psi(\kappa)\rangle = e^{-\hat{\kappa}}|\Psi_0^{CASSCF}\rangle$$

$$E_0^{CASSCF} = \min_{\kappa}\langle\Psi(\kappa)|\hat{H}|\Psi(\kappa)\rangle \overset{\kappa=0}{=} \langle\Psi_0^{CASSCF}|\hat{H}|\Psi_0^{CASSCF}\rangle$$

$$\Downarrow$$

$$\left.\frac{\partial\langle\Psi(\kappa)|\hat{H}|\Psi(\kappa)\rangle}{\partial\kappa_{PQ}}\right|_{\kappa=0} = 0$$

Spin-orbital rotation in the vicinity of the minimizing CASSCF wave function

Will be investigated further during the exercise session…

Generalised Brillouin theorem

$$\left.\frac{\partial\langle\Psi(\kappa)|\hat{H}|\Psi(\kappa)\rangle}{\partial\kappa_{PQ}}\right|_{\kappa=0} = 0$$

Complements

Spin-orbital rotation in first quantization

$$|\varphi_{P(\kappa)}\rangle = \sum_Q \mathcal{U}_{QP}(\kappa)\,|\varphi_Q\rangle$$

$$\mathcal{U}_{QP}(\kappa) = \left(e^{-\kappa}\right)_{QP}$$

Spin-orbital rotation in first quantization

$$|\varphi_{P(\kappa)}\rangle = \sum_Q \mathcal{U}_{QP}(\kappa)|\varphi_Q\rangle$$

$$\mathcal{U}_{QP}(\kappa) = \left(e^{-\kappa}\right)_{QP}$$

$$\left(\kappa^\dagger\right)_{PQ} = (-\kappa)_{PQ} = \kappa^*_{QP} = -\kappa_{PQ} \longrightarrow \kappa \equiv \left\{\kappa_{PQ}\right\}_{P<Q}$$

Spin-orbital rotation in second quantization

$$|\varphi_{P(\kappa)}\rangle = \sum_{Q} \left(e^{-\kappa}\right)_{QP} |\varphi_Q\rangle$$

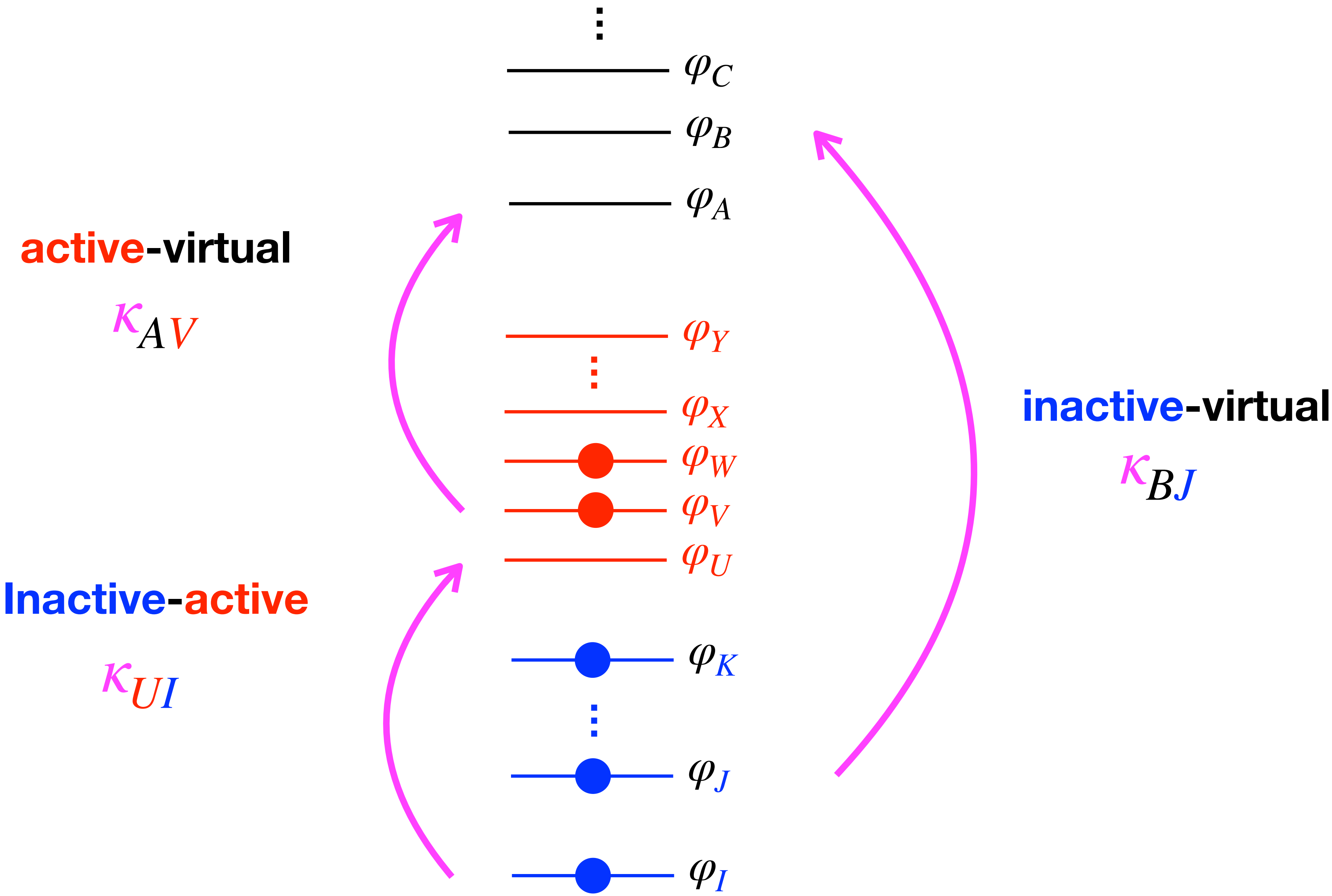
$\Updownarrow$

$$\hat{a}^{\dagger}_{P(\kappa)} = \sum_{Q} \left(e^{-\kappa}\right)_{QP} \hat{a}^{\dagger}_{Q}$$

$\Updownarrow$

$$\hat{a}^{\dagger}_{P(\kappa)} = e^{-\hat{\kappa}} \hat{a}^{\dagger}_{P} e^{+\hat{\kappa}}$$ **where** $$\hat{\kappa} = \sum_{PQ} \kappa_{PQ} \hat{a}^{\dagger}_{P} \hat{a}_{Q}$$

$$|\Psi(\kappa)\rangle = e^{-\hat{\kappa}}|\Psi_0^{CASSCF}\rangle = \left(1-\hat{\kappa}+\ldots\right)|\Psi_0^{CASSCF}\rangle = \left(1-\sum_{PQ}\kappa_{PQ}\,\hat{a}_P^{\dagger}\hat{a}_Q+\ldots\right)|\Psi_0^{CASSCF}\rangle$$



State-Averaged CASSCF orbitals

$$\left\{ |\Psi_n(\kappa)\rangle = e^{-\hat{\kappa}} |\Psi_n^{CASSCF}\rangle \right\}_{n=0,1,2,\ldots}$$

State-Averaged CASSCF orbitals

$$\left\{ |\Psi_n(\kappa)\rangle = e^{-\hat{\kappa}} |\Psi_n^{CASSCF}\rangle \right\}_{n=0,1,2,\ldots}$$

Variational principle for an ***ensemble*** of ground and excited states:

$$\sum_n \mathtt{w}_n E_n \underset{\substack{\mathtt{w}_0 \geq \mathtt{w}_1 \geq \mathtt{w}_2 \geq \ldots \geq 0 \\ \langle \Psi_n | \Psi_m \rangle = \delta_{mn}}}{\leq} \sum_n \mathtt{w}_n \langle \Psi_n | \hat{H} | \Psi_n \rangle$$

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
A. K. Theophilou, in The Single Particle Density in Physics and Chemistry, edited by N. H. March and B. M. Deb (Academic Press, 1987), pp. 210–212.
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2805 (1988).*

State-Averaged CASSCF orbitals

$$\left\{ |\Psi_n(\kappa)\rangle = e^{-\hat{\kappa}} |\Psi_n^{CASSCF}\rangle \right\}_{n=0,1,2,\ldots}$$

$$\downarrow$$

$$\kappa^{\{\mathtt{w}_n\}} = \mathrm{argmin}_{\kappa} \left\{ \sum_n \mathtt{w}_n \langle \Psi_n(\kappa) | \hat{H} | \Psi_n(\kappa) \rangle \right\}$$