Introduction to *ab initio* electronic structure theory

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Schrödinger equation for two-electron systems

- Two-electron wavefunction: $\Psi(\mathbf{r}_1, \mathbf{r}_2)$

  where $\mathbf{r}_1 \equiv (x_1, y_1, z_1)$ et $\mathbf{r}_2 \equiv (x_2, y_2, z_2)$ are space coordinates of electron 1 and 2.

- Schrödinger equation: $\boxed{\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)}$

  where the two-electron Hamiltonian equals $\hat{H} = \hat{T} + \hat{V} + \hat{W}_{\text{ee}}$ with

$$\hat{T} \equiv -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_2}$$ ⟵ kinetic energy operator

$$\hat{V} \equiv \Big(v(\mathbf{r}_1) + v(\mathbf{r}_2)\Big)\times$$ ⟵ nuclear attraction potential operator

$$\hat{W}_{\text{ee}} \equiv \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\times$$ ⟵ electron-electron repulsion operator

Schrödinger equation for two-electron systems

- For an atom with atomic number Z: $v(\mathbf{r}) = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$ where $r = |\mathbf{r}|$.
- For the H_2 molecule: $v(\mathbf{r}) = -\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{R}_A|} - \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{R}_B|}$,

  where $\mathbf{R}_A$ and $\mathbf{R}_B$ are the position vectors of the two nuclei.

Particular case of "non-interacting" electrons

- Let us assume that electrons do not repel each other (!) $\longrightarrow$ $\hat{W}_{\rm ee} \equiv 0$.

- If one can solve the following one-electron Schrödinger equation,

$$\Big(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + v(\mathbf{r})\Big)\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r}),$$

then a trivial solution to the Schrödinger equation for two electrons is

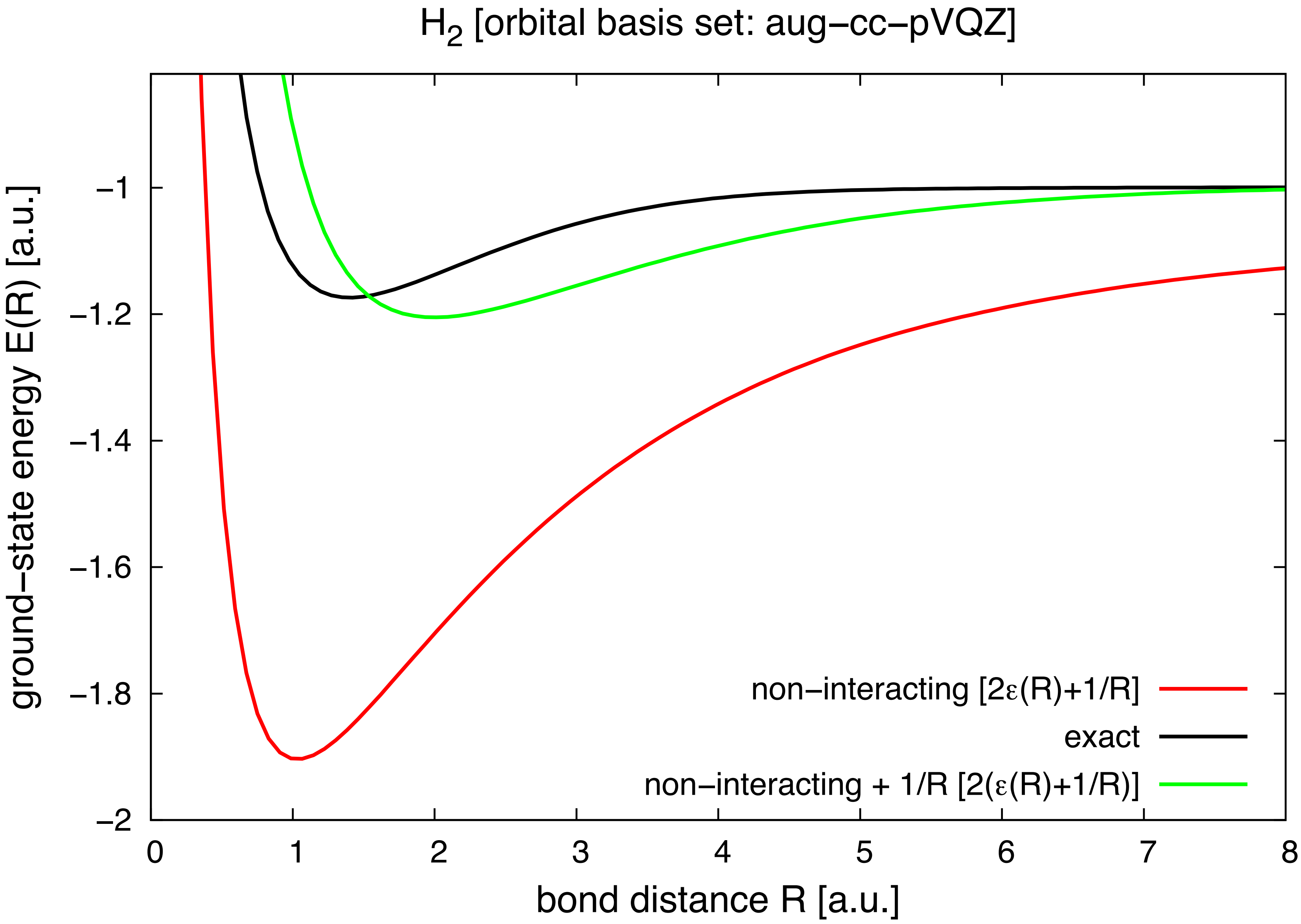
$$\boxed{\Psi(\mathbf{r}_1,\mathbf{r}_2) = \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) \quad \text{and} \quad E = 2\varepsilon}.$$

<u>Proof</u>:

$$\Big(\hat{T}+\hat{V}\Big)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) = \varphi(\mathbf{r}_2)\left[\left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_1} + v(\mathbf{r}_1)\right)\varphi(\mathbf{r}_1)\right] + \varphi(\mathbf{r}_1)\left[\left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_2} + v(\mathbf{r}_2)\right)\varphi(\mathbf{r}_2)\right]$$

$$= \varphi(\mathbf{r}_2)\varepsilon\varphi(\mathbf{r}_1) + \varphi(\mathbf{r}_1)\varepsilon\varphi(\mathbf{r}_2)$$

$$= 2\varepsilon\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$$


H_2 [orbital basis set: aug−cc−pVQZ]
ground−state energy E(R) [a.u.]
−1
−1.2
−1.4
−1.6
−1.8
−2
0
1
2
3
4
5
6
7
8
bond distance R [a.u.]
non−interacting [2ε(R)+1/R]
exact
non−interacting + 1/R [2(ε(R)+1/R)]

Returning to interacting electrons ...

- Describing interacting electrons ($\hat{W}_{\rm ee} \neq 0$) is more complicated. Indeed, in this case, any exact solution $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ to the Schrödinger equation cannot be written as $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$:

$$\boxed{\Psi(\mathbf{r}_1, \mathbf{r}_2) \neq \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).}$$

Proof : Let us assume that we can find an orbital $\varphi(\mathbf{r})$ such that $\hat{H}\Big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\Big) = E\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ for any $\mathbf{r}_1$ and $\mathbf{r}_2$ values. Consequently,

$$\hat{W}_{\rm ee}\Big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\Big) = E\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) - \Big(\hat{T} + \hat{V}\Big)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).$$

Using the definition of the operators and dividing by $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ leads to

$$\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} = E + \frac{\hbar^2}{2m}\frac{\nabla^2_{\mathbf{r}_1}\varphi(\mathbf{r}_1)}{\varphi(\mathbf{r}_1)} + \frac{\hbar^2}{2m}\frac{\nabla^2_{\mathbf{r}_2}\varphi(\mathbf{r}_2)}{\varphi(\mathbf{r}_2)} - v(\mathbf{r}_1) - v(\mathbf{r}_2).$$

In the limit $\mathbf{r}_2 \rightarrow \mathbf{r}_1 = \mathbf{r}$, it comes $\forall\, \mathbf{r}, \quad E + \dfrac{\hbar^2}{m}\dfrac{\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})}{\varphi(\mathbf{r})} - 2v(\mathbf{r}) \rightarrow +\infty$ absurd !

Hartree–Fock approximation for two electrons

- A Hartree product $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ can be used as an approximation to the exact ground-state wavefunction.

- The "best" $\varphi(\mathbf{r})$ orbital is obtained by applying the variational principle and by restricting the minimization to Hartree products. Thus we obtain an approximate ground-state energy which is known as the Hartree–Fock (HF) energy:

$$\boxed{E_{\mathrm{HF}} = \min_{\varphi} \langle \Phi | \hat{H} | \Phi \rangle}$$

- Note that $\varphi(\mathbf{r})$ should be normalized so that $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is normalized.

EXERCISE: **(1)** Show that

$$\langle \Phi | \hat{H} | \Phi \rangle = 2\left(-\frac{\hbar^2}{2m} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \varphi(\mathbf{r}) \nabla^2_{\mathbf{r}} \varphi(\mathbf{r}) + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, v(\mathbf{r}) \varphi^2(\mathbf{r}) \right) + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \, \frac{e^2 \varphi^2(\mathbf{r}) \varphi^2(\mathbf{r}')}{4\pi\varepsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

Hartree–Fock approximation for two electrons

(2) By introducing the Lagrangian $\mathcal{L}[\varphi]=\langle\Phi|\hat{H}|\Phi\rangle+\varepsilon\big(1-\langle\varphi|\varphi\rangle\big)$,

show that the minimizing HF orbital $\varphi_{\mathrm{HF}}(\mathbf{r})$ fulfills the following self-consistent equation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}}+v(\mathbf{r})+\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}'\,\frac{e^2}{4\pi\varepsilon_0}\,\frac{\varphi^2_{\mathrm{HF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right)\varphi_{\mathrm{HF}}(\mathbf{r})=\varepsilon_{\mathrm{HF}}\varphi_{\mathrm{HF}}(\mathbf{r}).$$

(3) Show finally that $E_{\mathrm{HF}}=2\,\varepsilon_{\mathrm{HF}}-\displaystyle\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\frac{e^2\varphi^2_{\mathrm{HF}}(\mathbf{r})\varphi^2_{\mathrm{HF}}(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}$ ⟵ $E_{\mathrm{HF}}\neq 2\,\varepsilon_{\mathrm{HF}}$!

- In practice, the HF equation is solved approximately by decomposing the trial orbital $\varphi(\mathbf{r})$ in a finite basis of non-orthogonal (gaussian) atomic orbitals (AO) $\{\chi_p(\mathbf{r})\}_{p=1,\ldots,M}$:

$$\varphi(\mathbf{r})=\sum_{p=1}^{M}\tilde{C}_p\,\chi_p(\mathbf{r}).$$

The so-called molecular orbital (MO) coefficients $\{\tilde{C}_p\}_{p=1,\ldots,M}$ are then optimized variationally.

Electron correlation

- Let us stress that HF is an approximate method. In the following, we shall refer to the difference between the exact ground-state energy E_0 and the HF energy as the correlation energy $E_{\rm c}$:

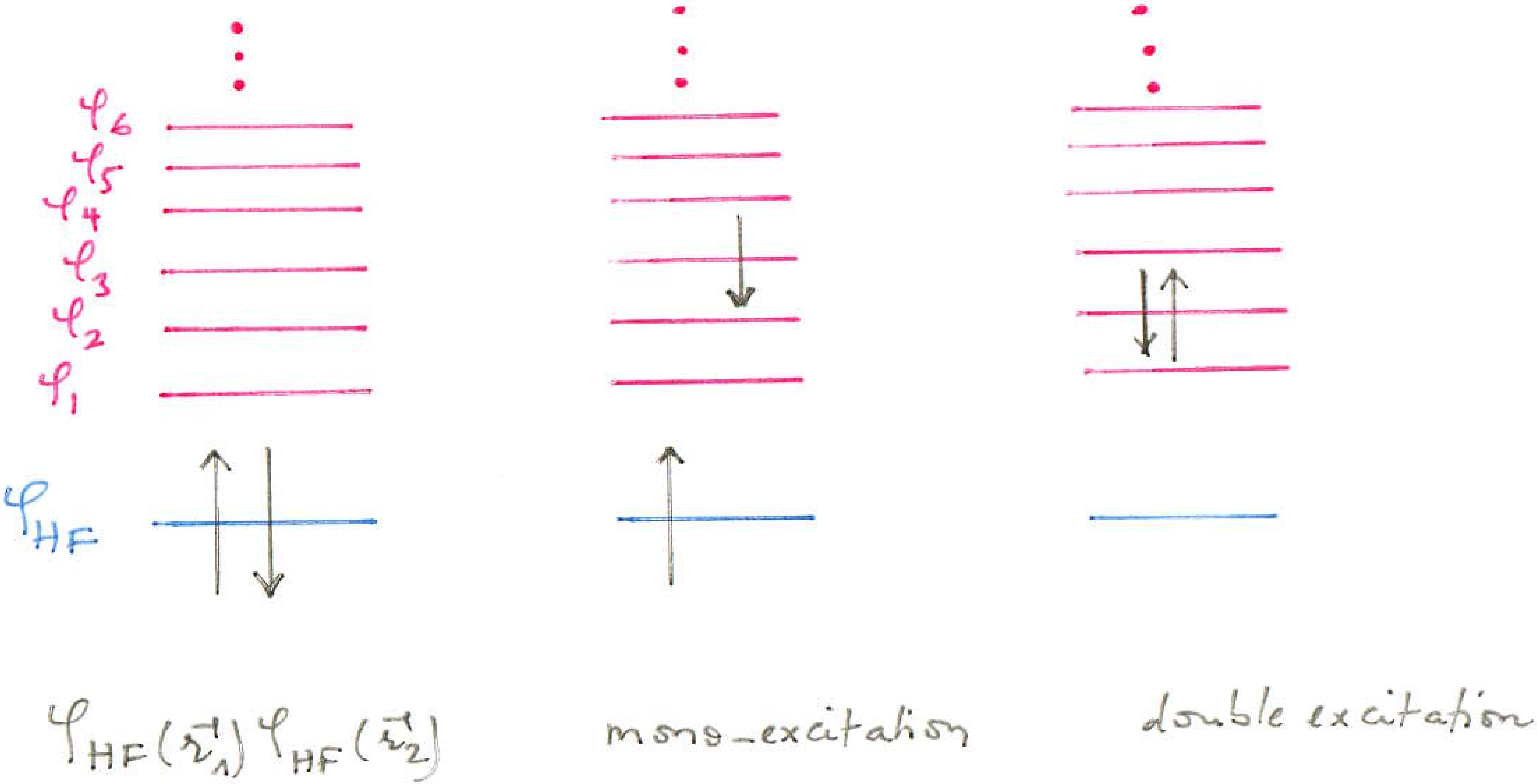
$$E_{\rm c} = E_0 - E_{\rm HF} < 0$$

- "Modelling electron correlation" means "going beyond the HF approximation".
- Note that the doubly-occupied HF orbital $\varphi_{\rm HF}(\mathbf{r})$ is an eigenfunction of the so-called Fock operator

$$\hat{f} \equiv -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} + \left(v(\mathbf{r}) + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}' \, \frac{e^2}{4\pi\varepsilon_0} \frac{\varphi^2_{\rm HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right) \times$$

- Of course, this operator has many other eigenfunctions $\Big\{\varphi_i(\mathbf{r})\Big\}_{i=1,2,\ldots}$ with energies $\Big\{\varepsilon_i\Big\}_{i=1,2,\ldots}$ that are higher than $\varepsilon_{\rm HF}$. These orbitals are referred to as virtual orbitals (or just virtuals).
- Frontier orbitals: $\varphi_{\rm HF}(\mathbf{r})$ is referred to as HOMO (Highest Occupied Molecular Orbital) and $\varphi_1(\mathbf{r})$ is the LUMO (Lowest Unoccupied Molecular Orbital).

Electron correlation

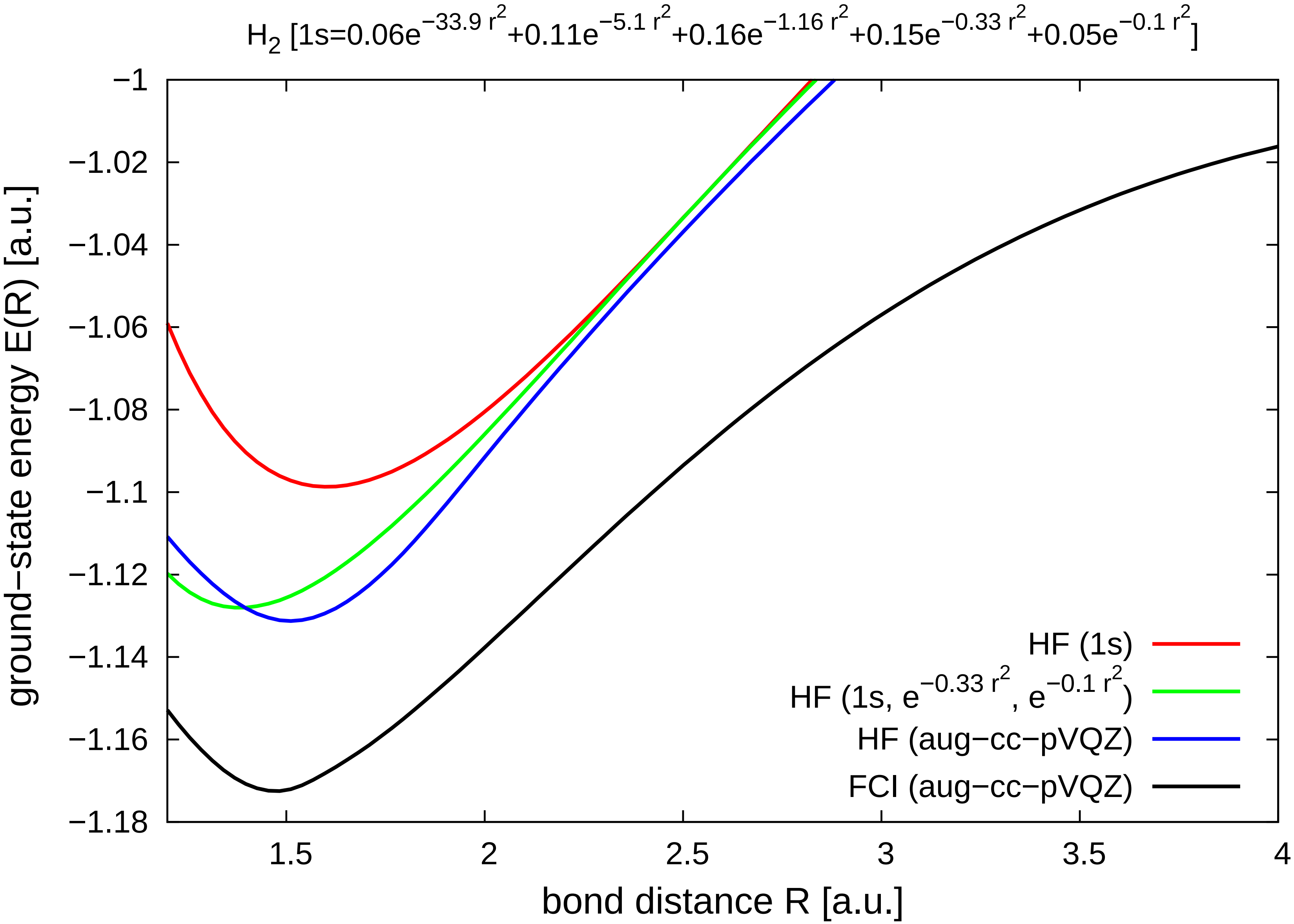


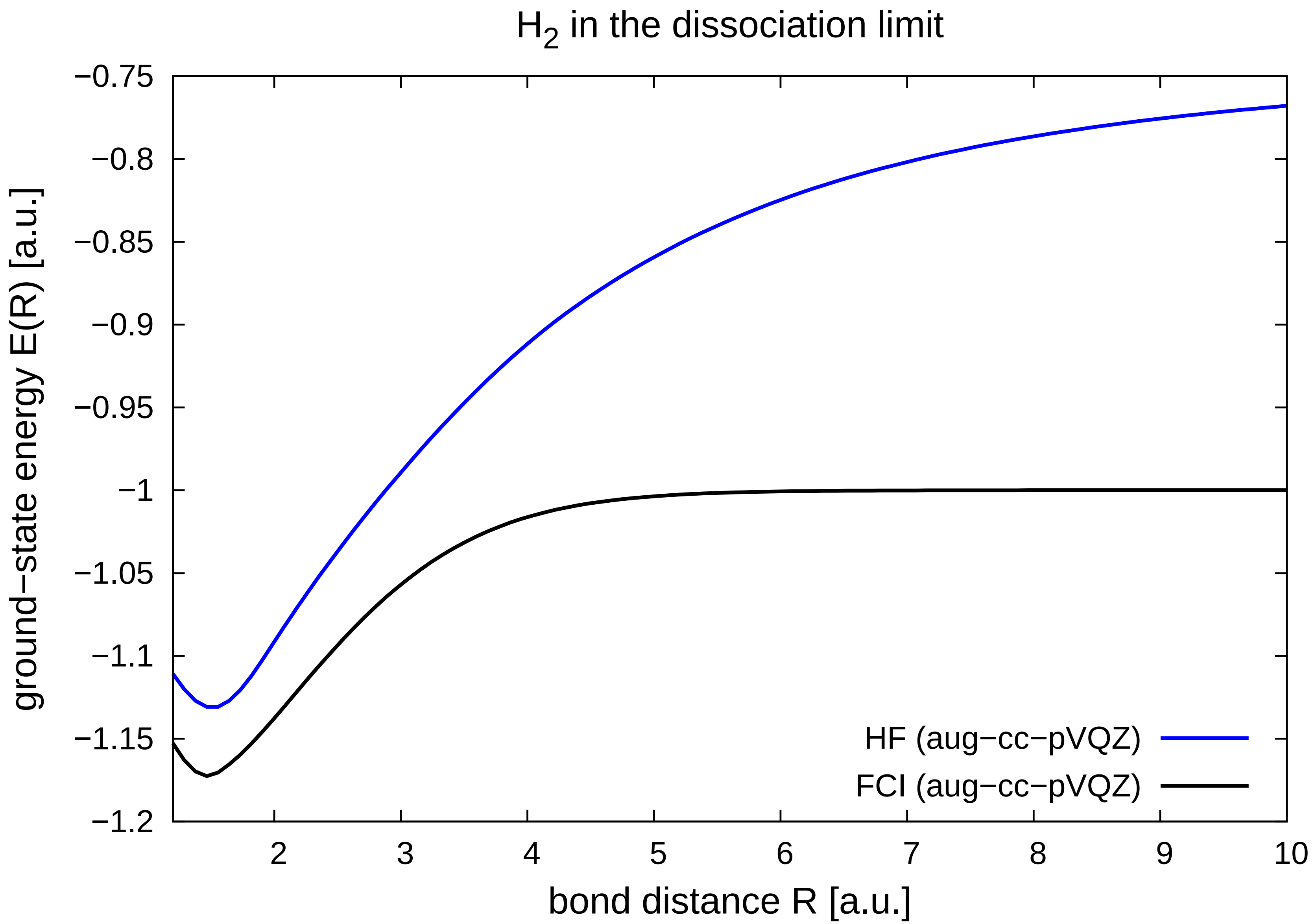
Electron correlation

- Virtual orbitals can actually be used as a basis for modelling electron correlation, thus leading to the following (better) approximation to the exact ground-state wavefunction,

$$\begin{aligned}\Psi_0(\mathbf{r}_1,\mathbf{r}_2) \approx\ & \varphi_{\mathrm{HF}}(\mathbf{r}_1)\varphi_{\mathrm{HF}}(\mathbf{r}_2) && \longleftarrow \text{ HF wavefunction}\\ &+\sum_{i\geq 1} C_i\Big(\varphi_{\mathrm{HF}}(\mathbf{r}_1)\varphi_i(\mathbf{r}_2) \ + \ \varphi_i(\mathbf{r}_1)\varphi_{\mathrm{HF}}(\mathbf{r}_2)\Big) && \longleftarrow \text{ single excitation}\\ &+\sum_{j\geq i\geq 1} C_{ij}\Big(\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \ + \ \varphi_j(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)\Big) && \longleftarrow \text{ double excitation}\end{aligned}$$

- The coefficients C_i and C_{ij} are optimized variationally.
- If the distribution of **ALL** the electrons (two here) in **ALL** the orbitals (occupied and virtuals) is considered, the method is referred to as Full Configuration Interaction (FCI).
- The FCI method is exact in a given finite basis of atomic orbitals. In this case, the FCI wavefunction is of course not equal to the exact wavefunction $\Psi_0(\mathbf{r}_1,\mathbf{r}_2)$. The latter can only be reached, in principle, by using an infinite basis.


H_2 [1s=0.06e$^{-33.9 r^2}$+0.11e$^{-5.1 r^2}$+0.16e$^{-1.16 r^2}$+0.15e$^{-0.33 r^2}$+0.05e$^{-0.1 r^2}$]
ground−state energy E(R) [a.u.]
−1
−1.02
−1.04
−1.06
−1.08
−1.1
−1.12
−1.14
−1.16
−1.18
1.5
2
2.5
3
3.5
4
bond distance R [a.u.]
HF (1s)
HF (1s, e$^{-0.33 r^2}$, e$^{-0.1 r^2}$)
HF (aug−cc−pVQZ)
FCI (aug−cc−pVQZ)


H2 in the dissociation limit
ground−state energy E(R) [a.u.]
−0.75
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
2
3
4
5
6
7
8
9
10
bond distance R [a.u.]
HF (aug−cc−pVQZ)
FCI (aug−cc−pVQZ)