Introduction to quantum chemistry

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Electronic Hamiltonian, SI and atomic units

- We work within the *Born–Oppenheimer* approximation where the electronic structure is described for *fixed* nuclei positions.
- A physical N-electron wavefunction $\Psi \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is a function of the electron positions $\mathbf{r}_i \equiv (x_i, y_i, z_i)$ [spin will be introduced later on] that fulfils the *Schrödinger equation* $\boxed{\hat{H}\Psi = E\Psi}$.
- The N-electron *Hamiltonian operator* can be written as

$$\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne}$$

$$\hat{T} \equiv \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \qquad \rightarrow \text{ kinetic energy}$$

$$\hat{W}_{\rm ee} = \frac{1}{2}\sum_{i \neq j}^{N} \hat{w}_{\rm ee}(i,j) \qquad \text{with} \quad \hat{w}_{\rm ee}(i,j) \equiv \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \times \qquad \rightarrow \text{ electron-electron repulsion}$$

$$\hat{V}_{\rm ne} = \sum_{i=1}^{N} \hat{v}_{\rm ne}(i) \qquad \text{with} \quad \hat{v}_{\rm ne}(i) \equiv -\sum_{A}^{\rm nuclei} \frac{Z_A e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{R}_A|} \times \qquad \rightarrow \text{ electron-nuclei attraction}$$

Electronic Hamiltonian, SI and atomic units

- Hydrogen atom ($N = 1$):

$$\hat{H} \rightarrow -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}} \times \,,$$

$E \rightarrow \boxed{E_n = -\frac{E_{\mathrm{I}}}{n^2}}$ where the ionization energy equals $E_{\mathrm{I}} = \frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} \approx 13.6\,\mathrm{eV}$.

The ground-state wavefunction ($n = 1$) equals $\boxed{\Psi_{1\mathrm{s}}(x,y,z) = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-\sqrt{x^2+y^2+z^2}/a_0}}$ where

Bohr's radius equals $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \approx 0.529$ Å.

- Working with so-called "atomic units" simply consists in using unitless energies $\tilde{E} = E/(2E_{\mathrm{I}})$ and coordinates $\tilde{x} = x/a_0$, $\tilde{y} = y/a_0$, $\tilde{z} = z/a_0$.

- The ground-state energy of the hydrogen atom is therefore -0.5 in atomic units.

- Returning to the general N-electron problem, the Schrödinger equation in atomic units is obtained from $\dfrac{\hat{H}\Psi}{2E_{\mathrm{I}}} = \tilde{E}\Psi$ where the change of variables $\mathbf{r}_i = a_0\tilde{\mathbf{r}}_i \; (i = 1, 2, \ldots, N)$ is made [*see the complements*].

- Eventually, $\tilde{\mathbf{r}}_i$ and $\tilde{E}$ will simply be denoted $\mathbf{r}_i$ and E, respectively, thus leading to

$$\hat{H}\Psi = E\Psi,$$

where

$$\boxed{\hat{H} \equiv -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} \; + \; \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{r_{ij}}\times \; + \; \sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)\times}$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad \text{and} \quad v_{\mathrm{ne}}(\mathbf{r}_i) = -\sum_{A}^{\text{nuclei}}\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}.$$

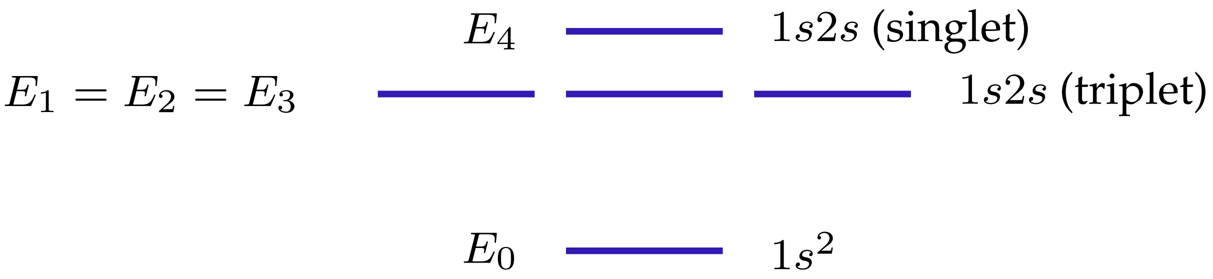
- We will systematically *normalize* the solutions, *i.e.*, we impose the following normalization condition:

$$\langle\Psi|\Psi\rangle = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \, |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 = 1.$$

Connecting theory to experiment

- The quantities we will mainly focus on are the ground-state E_0 and excited-state $\{E_I\}_{I>0}$ energies.

- In the following, we will assume (for simplicity) that the ground state is not degenerate like, for example, in the helium atom:



- Electronic excitation energies $\omega_I = E_I - E_0$ can be measured (UV/visible spectroscopy).

- The ground-state energy E_0 is also interesting in itself. Indeed, it gives access to equilibrium geometries, vibrational frequencies, static response properties (polarizabilities, magnetic susceptibilities, ...)

Vibrational frequencies in diatomics

- Let us consider the more general *molecular* problem where both nuclei and electrons are treated quantum-mechanically. For simplicity, we will ignore rotation and assume that the mass M of nucleus B is much larger than the mass m of nucleus A ($m << M$) thus leading to the Schrödinger equation for the molecule

  $$\hat{H}^{\mathrm{mol}}\Psi^{\mathrm{mol}}(R,\mathbf{q}) = E^{\mathrm{mol}}\Psi^{\mathrm{mol}}(R,\mathbf{q})$$

  where the molecular Hamiltonian equals in atomic units

  $$\hat{H}^{\mathrm{mol}} \equiv -\frac{1}{2m}\frac{\partial^2}{\partial R^2} + \frac{Z_A Z_B}{R} + \hat{H}(R).$$

  R is the distance between A and B, $\hat{H}(R)$ is the electronic Hamiltonian (simply referred to as $\hat{H}$ on the previous slides) that depends explicitly on R, and the positions of all the electrons are collected in $\mathbf{q} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$.

- Within the Born-Oppenheimer approximation, the molecular wavefunction is decomposed as follows, $\Psi^{\mathrm{mol}}(R,\mathbf{q}) = \chi(R)\Psi(R,\mathbf{q})$, where

  $$\hat{H}(R)\Psi(R,\mathbf{q}) = E(R)\Psi(R,\mathbf{q})$$

- Within the so-called adiabatic approximation, derivatives of the electronic wavefunction with respect to nuclear displacements are neglected: $\partial\Psi(R,\mathbf{q})/\partial R \approx 0 \approx \partial^2\Psi(R,\mathbf{q})/\partial R^2$.
- Such an approximation is in principle relevant when the molecule is close to equilibrium.
- Therefore, the *nuclear wavefunction* fulfills the following Schrödinger equation

$$\left[-\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V(R)\times\right]\chi(R) = E^{\mathrm{mol}}\chi(R),$$

where $\boxed{V(R) = E(R) + \frac{Z_A Z_B}{R}}$.

- $V(R)$ is the potential interaction energy between the two nuclei in the field of the electrons.
- From a classical mechanics point of view, the force $F(R) = -\mathrm{d}V(R)/\mathrm{d}R$ is applied to nucleus A.
- The equilibrium distance R_0 is such that $F(R) < 0$ when $R > R_0$ and $F(R) > 0$ when $R < R_0$.
- $F(R)$ being continuous implies $\boxed{F(R_0) = 0 = \left.\frac{\mathrm{d}V(R)}{\mathrm{d}R}\right|_{R=R_0} = 0}$ ← equilibrium structure!

- Note that an equilibrium structure is obtained when R_0 minimizes $V(R)$.
- In the general case (larger molecules), R will be a reaction coordinate and maxima of $V(R)$ will correspond to transition states. Once a transition state is reached, the molecule will switch to another equilibrium state that corresponds to a local minimum of $V(R)$.
- Let us consider fluctuations $x = R - R_0$ around the equilibrium bond distance R_0. From the Taylor expansion through second order in x,

$$V(R) = V(R_0 + x) \approx V(R_0) + \frac{1}{2}\left(\left.\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right|_{R=R_0} \right) x^2,$$

we recover the Schrödinger equation for the harmonic oscillator with frequency $\omega = \sqrt{\frac{1}{m}\left.\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right|_{R=R_0}}$ or, equivalently, with *spring constant* $k = \left.\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right|_{R=R_0}$,

$$\boxed{\left[-\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\times\right]\varphi(x) = \mathcal{E}_{\mathrm{vib}} \times \varphi(x)}$$

where $\varphi(x) = \chi(R_0 + x)$ and $\mathcal{E}_{\mathrm{vib}} = E^{\mathrm{mol}} - V(R_0)$.

- This approximation is known as the harmonic approximation.

- The exact solutions to this problem are known:

$$\boxed{\mathcal{E}_{\rm vib} \equiv \omega\left(n+\frac{1}{2}\right)} \Leftrightarrow E^{\rm mol} \equiv E^{\rm mol}_n = V(R_0) + \omega\left(n+\frac{1}{2}\right), \quad \text{where} \quad n = 0, 1, 2, \ldots$$

- The vibrational frequency ω can be measured by infrared spectroscopy.

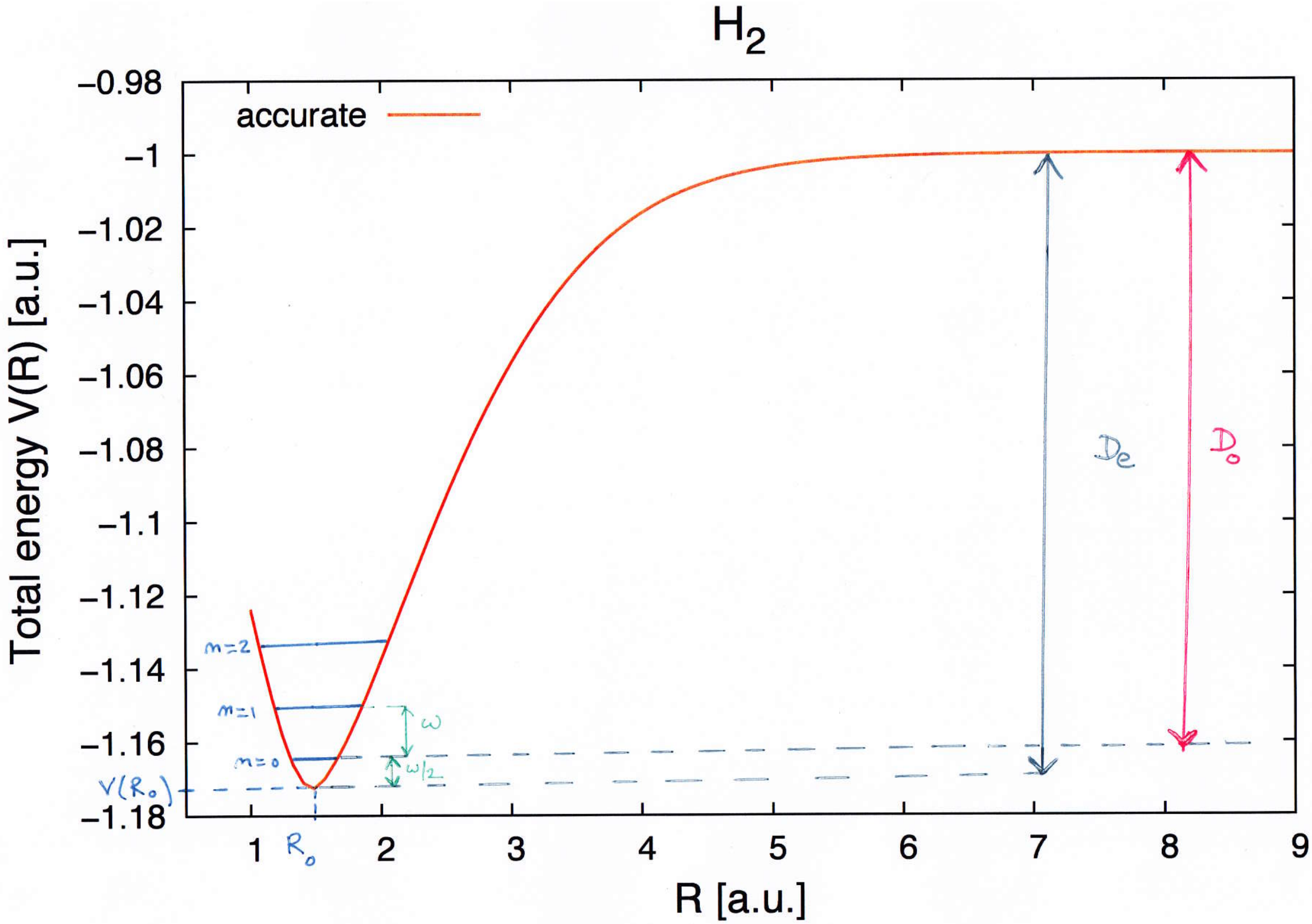
- The equilibrium bond distance R_0 can be measured, for example, by microwave spectroscopy (rotational spectroscopy).

- When the molecule is in its ground vibrational state ($n = 0$) its energy equals

$$E^{\rm mol}_0 = V(R_0) + \underbrace{\frac{\omega}{2}}_{\text{zero point energy (ZPE)}}$$

- The binding energy can then be decomposed as follows:

$$D_0 = \underbrace{V(+\infty) - V(R_0)}_{D_e} - \frac{\omega}{2}$$


H$_2$
accurate
Total energy V(R) [a.u.]
R [a.u.]
−0.98
−1
−1.02
−1.04
−1.06
−1.08
−1.1
−1.12
−1.14
−1.16
−1.18
1
2
3
4
5
6
7
8
9
n=2
n=1
n=0
V(R₀)
R₀
ω
ω/2
Dₑ
D₀

(Rayleigh–Ritz) variational principle for the ground state

- Let $\{\Psi_I\}_{I=0,1,2,\ldots}$ denote the exact orthonormal electronic ground-state ($I=0$) and excited-state ($I>0$) wavefunctions:

$$\hat{H}|\Psi_I\rangle = E_I|\Psi_I\rangle, \quad \langle\Psi_I|\Psi_J\rangle = \delta_{IJ}.$$

- We assume for clarity that the ground state is non-degenerate: $E_I > E_0$ when $I > 0$.

- In this course, we will always use real algebra: $\langle\Psi|\Phi\rangle = \langle\Phi|\Psi\rangle^* = \langle\Phi|\Psi\rangle$.

- The exact ground-state energy can be expressed as $\boxed{E_0 = \min\limits_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_0|\hat{H}|\Psi_0\rangle}$

  where the minimization is restricted to normalized wavefunctions Ψ.

  Proof: $\forall\,\Psi,\ |\Psi\rangle = \sum\limits_I C_I|\Psi_I\rangle$ and $\langle\Psi|\hat{H}|\Psi\rangle - E_0\langle\Psi|\Psi\rangle = \sum\limits_I C_I^2\Big(E_I - E_0\Big) \geq 0.$

- Note that, if $\Psi \neq \Psi_0$, then $\boxed{\langle\Psi|\hat{H}|\Psi\rangle > E_0}$.

Schrödinger equation for two-electron systems

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

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

- 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 $\hat{H} = \hat{T} + \hat{V} + \hat{W}_{\mathrm{ee}}$, with

$$\hat{T} \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} \quad \longleftarrow \text{kinetic energy operator}$$

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

$$\hat{W}_{\mathrm{ee}} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\times \quad \longleftarrow \text{electron-electron repulsion operator}$$

Schrödinger equation for two-electron systems

- For an atom with atomic number Z: $v(\mathbf{r}) = -\dfrac{Z}{r}$
- For the H_2 molecule: $v(\mathbf{r}) = -\dfrac{1}{|\mathbf{r} - \mathbf{R}_A|} - \dfrac{1}{|\mathbf{r} - \mathbf{R}_B|}$

Particular case of "non-interacting" electrons

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

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

$$\Big(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r})\Big)\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r}),$$

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>:

$$\Big(\hat{T}+\hat{V}\Big)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) = \varphi(\mathbf{r}_2)\Bigg[\Big(-\frac{1}{2}\nabla^2_{\mathbf{r}_1} + v(\mathbf{r}_1)\Big)\varphi(\mathbf{r}_1)\Bigg] + \varphi(\mathbf{r}_1)\Bigg[\Big(-\frac{1}{2}\nabla^2_{\mathbf{r}_2} + v(\mathbf{r}_2)\Big)\varphi(\mathbf{r}_2)\Bigg]$$

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

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

Returning to interacting electrons...

- Describing interacting electrons ($\hat{W}_{\text{ee}} \not\equiv 0$) 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,

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

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

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = E + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_1}\varphi(\mathbf{r}_1)}{\varphi(\mathbf{r}_1)} + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_2}\varphi(\mathbf{r}_2)}{\varphi(\mathbf{r}_2)} - v(\mathbf{r}_1) - v(\mathbf{r}_2).$$

In the limit $\mathbf{r}_2 \rightarrow \mathbf{r}_1 = \mathbf{r}$, it comes $\quad \forall\,\mathbf{r}, \quad E + \dfrac{\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})}{\varphi(\mathbf{r})} - 2v(\mathbf{r}) \rightarrow +\infty$ 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 [*i.e.* $\int_{\mathbb{R}^3} d\mathbf{r}\,|\varphi(\mathbf{r})|^2=1$] so that $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ is normalized.

It can be shown that:

$$\textbf{(1)}\quad \langle\Phi|\hat{H}|\Phi\rangle=2\left(-\frac{1}{2}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\varphi(\mathbf{r})\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})+\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,v(\mathbf{r})\varphi^2(\mathbf{r})\right)+\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\frac{\varphi^2(\mathbf{r})\varphi^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Hartree–Fock approximation for two electrons

(2) The minimizing HF orbital $\varphi_{\mathrm{HF}}(\mathbf{r})$ fulfills the following self-consistent equation:

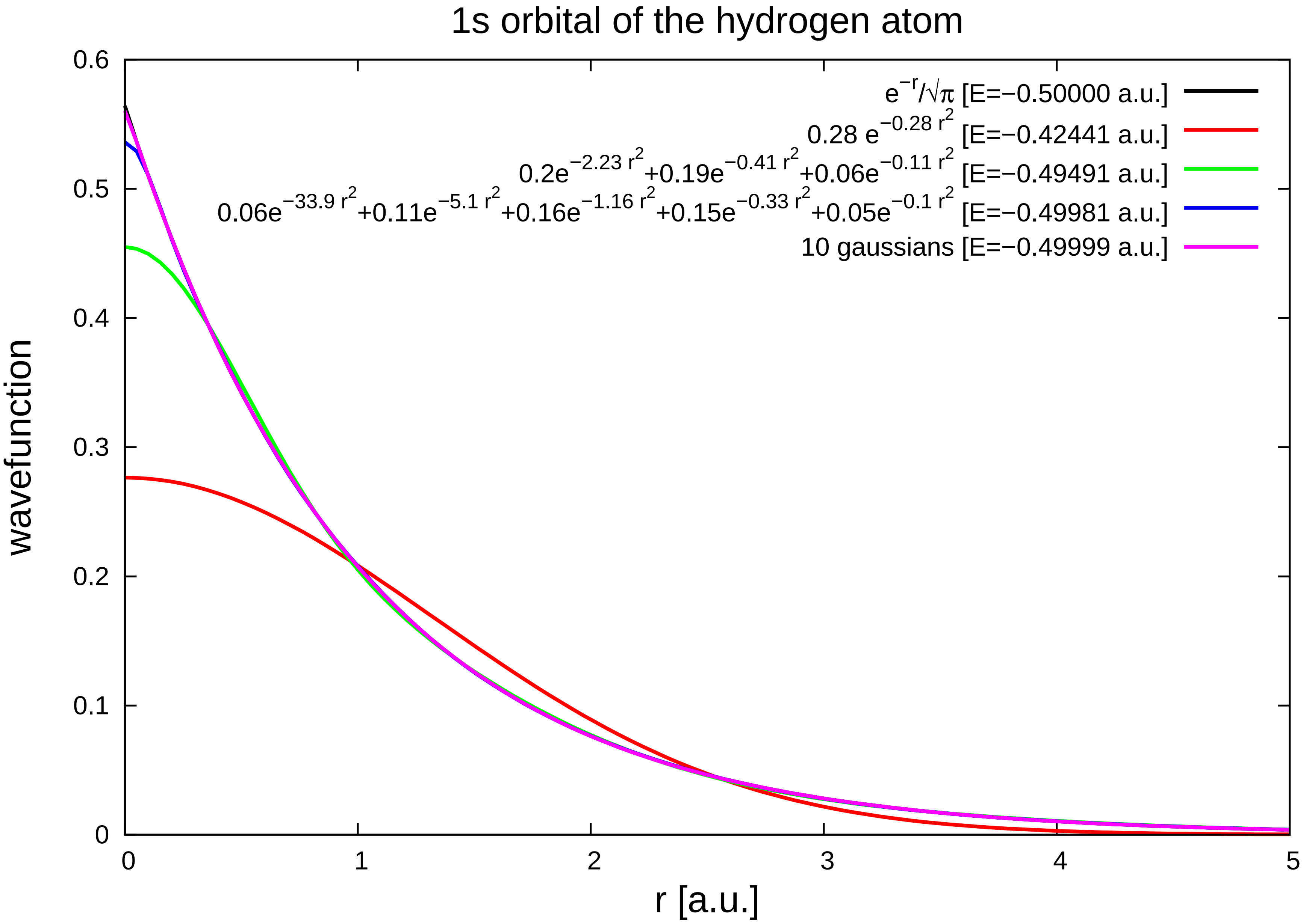
$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r}) + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}' \, \frac{\varphi^2_{\mathrm{HF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right)\varphi_{\mathrm{HF}}(\mathbf{r}) = \varepsilon_{\mathrm{HF}}\varphi_{\mathrm{HF}}(\mathbf{r}).$$

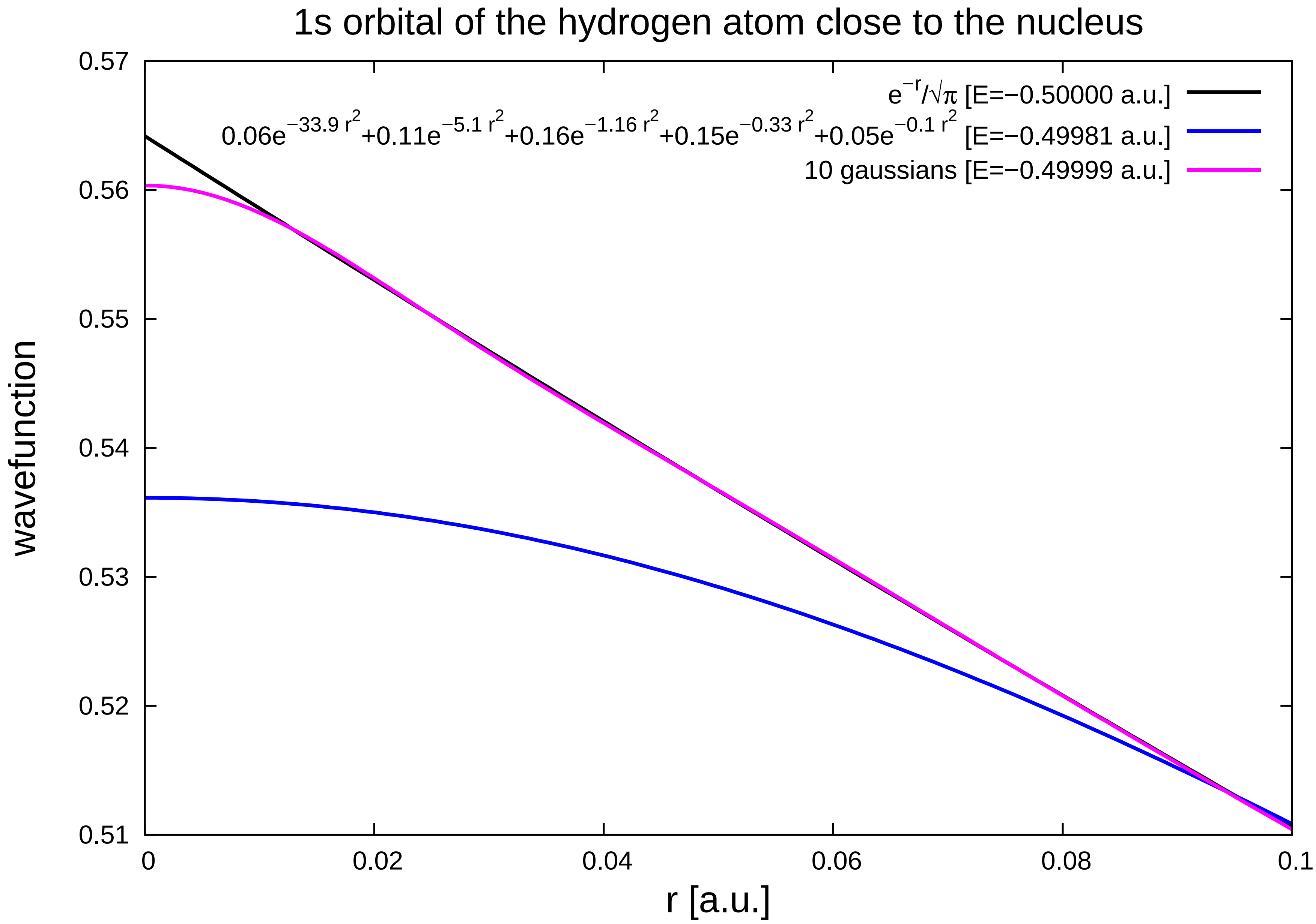
(3) $E_{\mathrm{HF}} = 2\,\varepsilon_{\mathrm{HF}} - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \, \frac{\varphi^2_{\mathrm{HF}}(\mathbf{r})\varphi^2_{\mathrm{HF}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ $\longleftarrow$ $E_{\mathrm{HF}} \neq 2\,\varepsilon_{\mathrm{HF}}!$

- 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) $\left\{\chi_p(\mathbf{r})\right\}_{p=1,\ldots,M}$:

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

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


1s orbital of the hydrogen atom
$e^{-r}/\sqrt{\pi}$ [E=−0.50000 a.u.]
$0.28\,e^{-0.28\,r^2}$ [E=−0.42441 a.u.]
$0.2e^{-2.23\,r^2}+0.19e^{-0.41\,r^2}+0.06e^{-0.11\,r^2}$ [E=−0.49491 a.u.]
$0.06e^{-33.9\,r^2}+0.11e^{-5.1\,r^2}+0.16e^{-1.16\,r^2}+0.15e^{-0.33\,r^2}+0.05e^{-0.1\,r^2}$ [E=−0.49981 a.u.]
10 gaussians [E=−0.49999 a.u.]
wavefunction
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
r [a.u.]


1s orbital of the hydrogen atom close to the nucleus
$e^{-r}/\sqrt{\pi}$ [E=−0.50000 a.u.]
$0.06e^{-33.9\,r^2}+0.11e^{-5.1\,r^2}+0.16e^{-1.16\,r^2}+0.15e^{-0.33\,r^2}+0.05e^{-0.1\,r^2}$ [E=−0.49981 a.u.]
10 gaussians [E=−0.49999 a.u.]
wavefunction
0.57
0.56
0.55
0.54
0.53
0.52
0.51
0
0.02
0.04
0.06
0.08
0.1
r [a.u.]

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 $E_{\rm c}$:

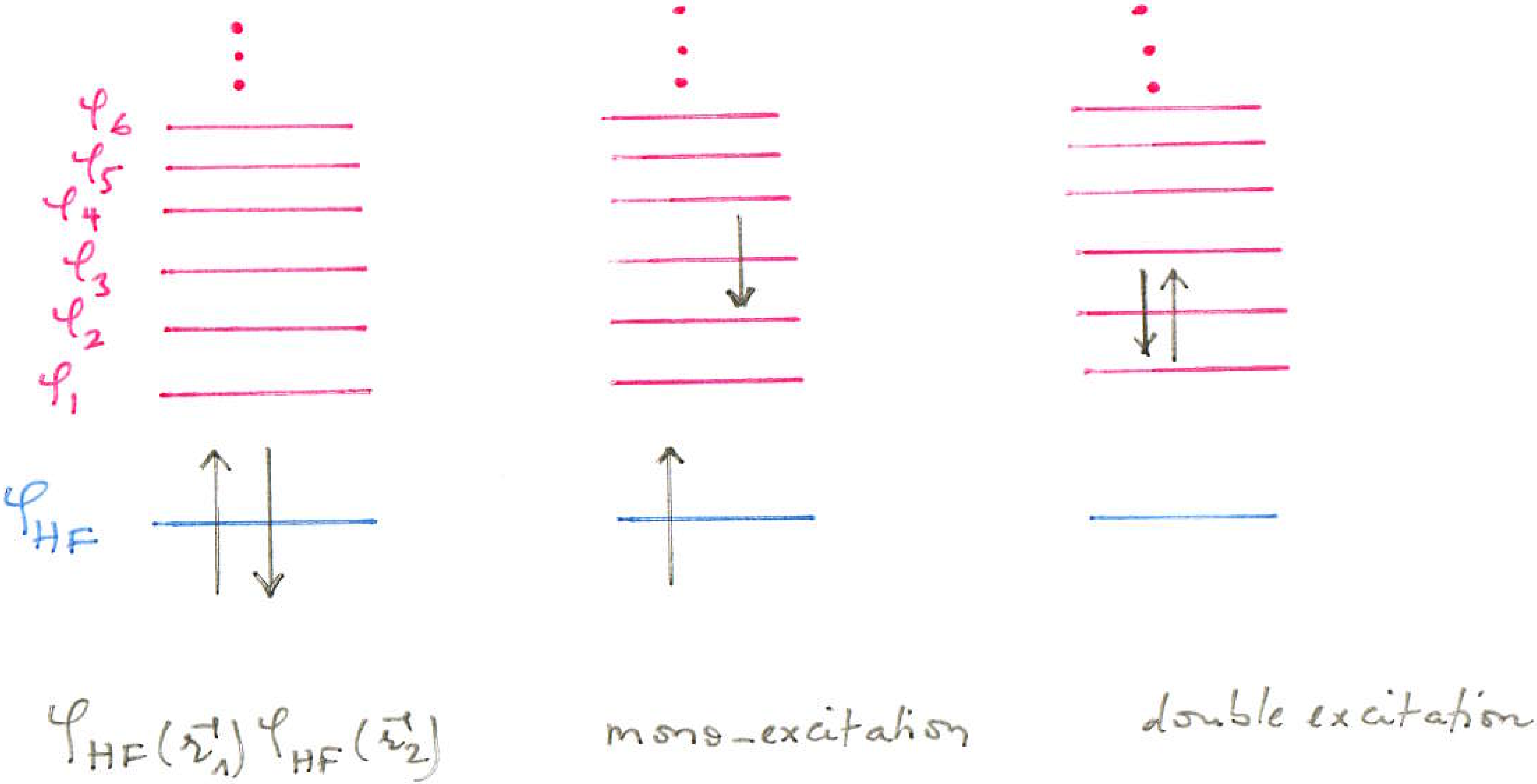
$$E_{\rm c} = E_0 - E_{\rm HF} < 0.$$

- "Modelling electron correlation" means "going beyond the HF approximation".
- The doubly-occupied HF orbital $\varphi_{\rm HF} \equiv \varphi_0$ is an eigenfunction of the so-called Fock operator:

$$\hat{f} \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}} + \left(v(\mathbf{r}) + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}' \, \frac{\varphi^2_{\rm HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right) \times$$

- Of course, this operator has many other eigenfunctions $\left\{\varphi_i(\mathbf{r})\right\}_{i=1,2,\ldots}$ with energies $\left\{\varepsilon_i\right\}_{i=1,2,\ldots}$ that are higher than $\varepsilon_{\rm HF} \equiv \varepsilon_0$: $\boxed{\hat{f}\varphi_i(\mathbf{r}) \underset{i\geq 0}{=} \varepsilon_i\varphi_i(\mathbf{r})}$. The orbitals labeled as $i > 0$ are referred to as virtual orbitals (or just virtuals).
- Frontier orbitals: $\varphi_{\rm HF}(\mathbf{r})$ is referred to as the 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:

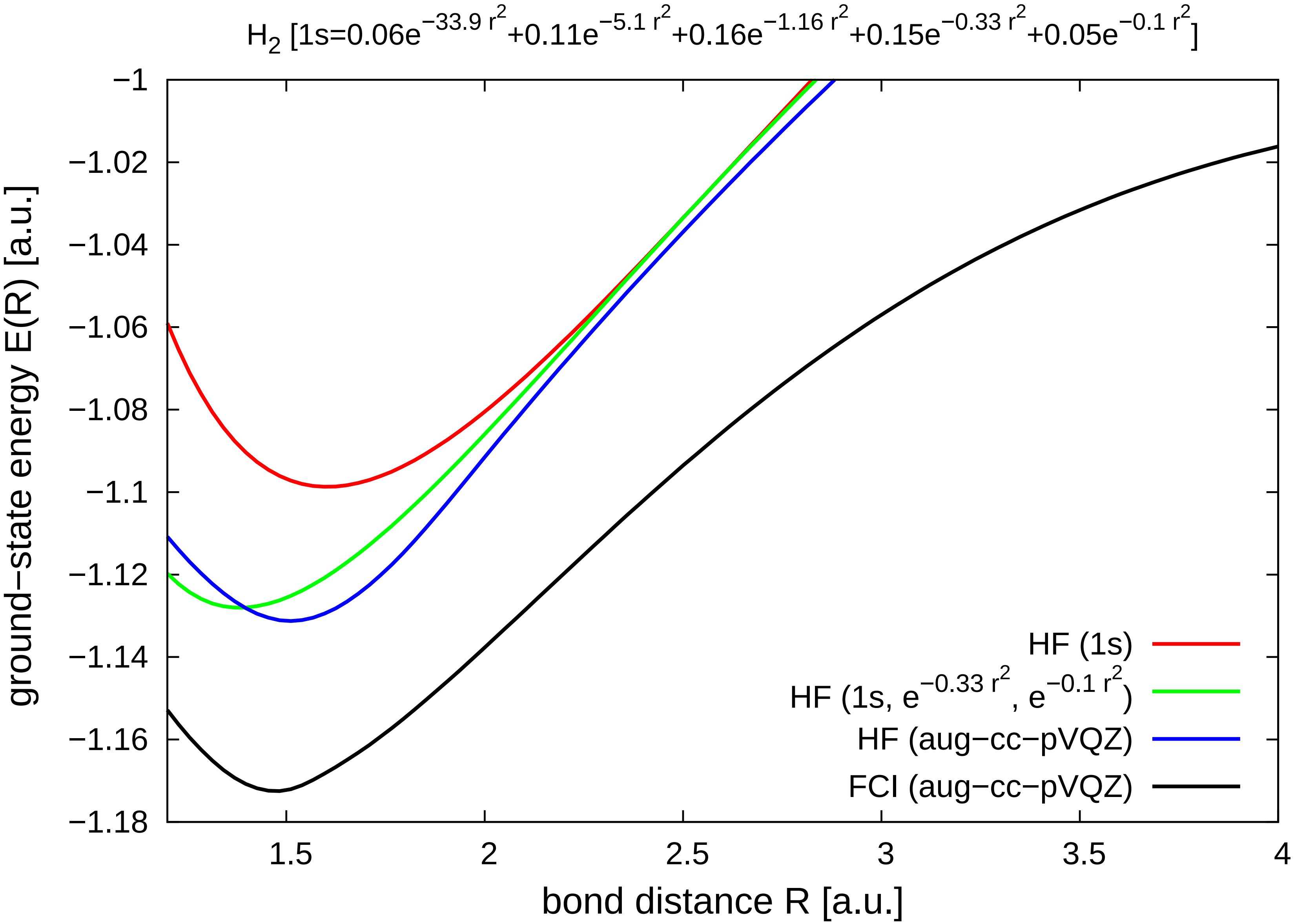
$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2) \approx \varphi_{\mathrm{HF}}(\mathbf{r}_1)\varphi_{\mathrm{HF}}(\mathbf{r}_2) \qquad \longleftarrow \quad \text{HF wavefunction}$$

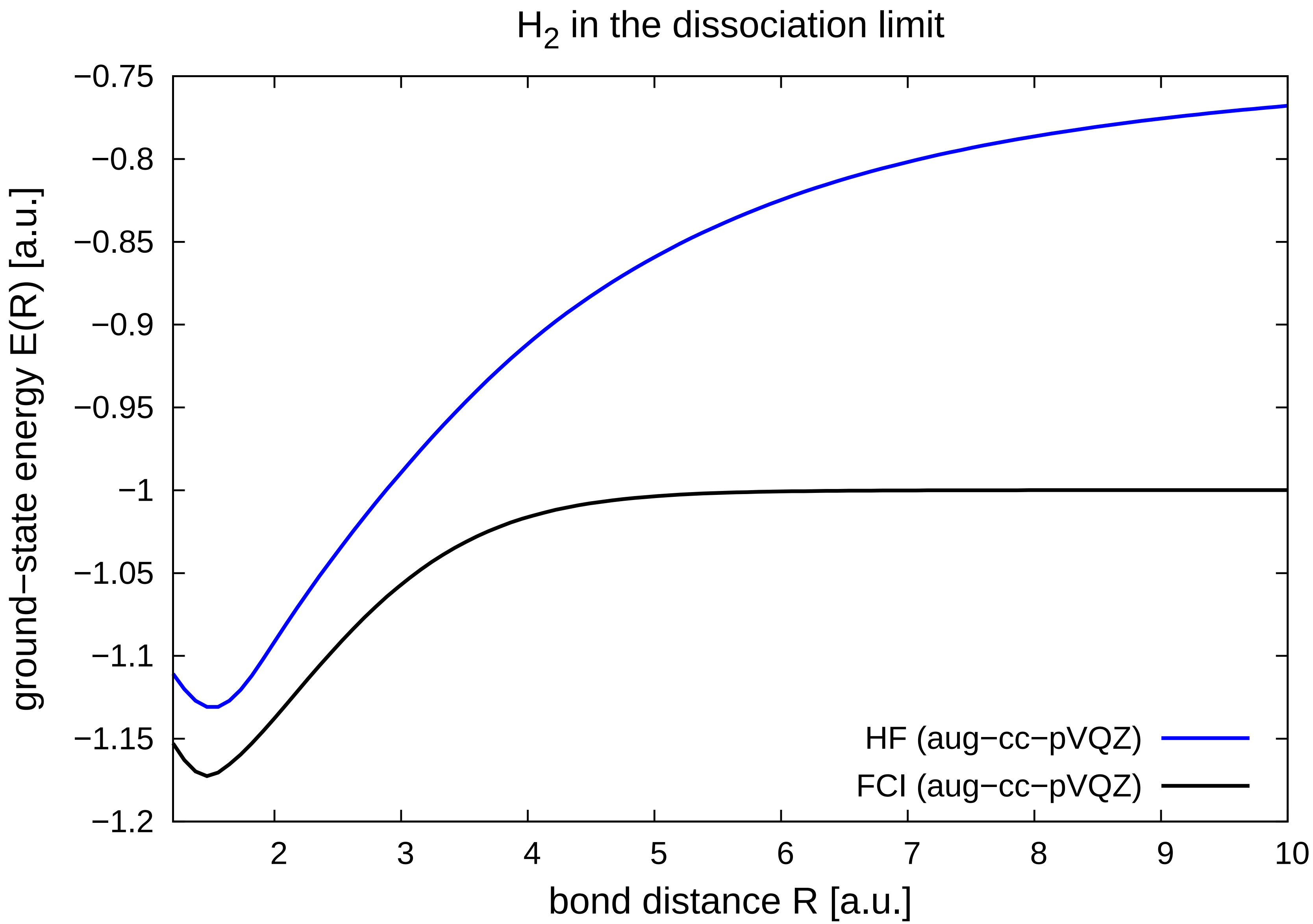
$$+\sum_{i\geq 1} C_i\Big(\varphi_{\mathrm{HF}}(\mathbf{r}_1)\varphi_i(\mathbf{r}_2) \;+\; \varphi_i(\mathbf{r}_1)\varphi_{\mathrm{HF}}(\mathbf{r}_2)\Big) \qquad \longleftarrow \quad \text{single excitation}$$

$$+\sum_{j\geq i\geq 1} C_{ij}\Big(\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \;+\; \varphi_j(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)\Big) \qquad \longleftarrow \quad \text{double excitation}$$

- The coefficients C_i and C_{ij} can be 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 true exact ground-state wave function $\Psi_0(\mathbf{r}_1,\mathbf{r}_2)$. The latter can only be reached, in principle, by using an *infinite-dimension* orbital (*i.e.*, one-electron wave function) 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.]
bond distance 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
HF (1s)
HF (1s, $e^{-0.33 r^2}$, $e^{-0.1 r^2}$)
HF (aug−cc−pVQZ)
FCI (aug−cc−pVQZ)


H$_2$ 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)

Complements

Electronic Hamiltonian, SI and atomic units

- Change of variables in the wavefunction:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\Psi(a_0\tilde{\mathbf{r}}_1,a_0\tilde{\mathbf{r}}_2,\ldots,a_0\tilde{\mathbf{r}}_N)=\tilde{\Psi}(\tilde{\mathbf{r}}_1,\tilde{\mathbf{r}}_2,\ldots,\tilde{\mathbf{r}}_N)=\tilde{\Psi}\left(\frac{\mathbf{r}_1}{a_0},\frac{\mathbf{r}_2}{a_0},\ldots,\frac{\mathbf{r}_N}{a_0}\right)$$

Using $\tilde{\Psi}$ rather than Ψ and the relations $2E_{\mathrm{I}}=\dfrac{\hbar^2}{m_e a_0^2}=\dfrac{e^2}{4\pi\varepsilon_0 a_0}$ leads to

$$\hat{T}/2E_{\mathrm{I}}\equiv\sum_{i=1}^{N}-\frac{a_0^2}{2}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)\equiv\sum_{i=1}^{N}-\frac{1}{2}\left(\frac{\partial^2}{\partial \tilde{x}_i^2}+\frac{\partial^2}{\partial \tilde{y}_i^2}+\frac{\partial^2}{\partial \tilde{z}_i^2}\right),$$

$$\hat{W}_{\mathrm{ee}}/2E_{\mathrm{I}}\equiv\frac{1}{2}\sum_{i\neq j}^{N}\frac{a_0}{r_{ij}}\times=\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{\tilde{r}_{ij}}\times,$$

$$\hat{V}_{\mathrm{ne}}/2E_{\mathrm{I}}\equiv\sum_{i=1}^{N}-\frac{Z_A a_0}{|\mathbf{r}_i-\mathbf{R}_A|}\times=\sum_{i=1}^{N}-\frac{Z_A}{|\tilde{\mathbf{r}}_i-\tilde{\mathbf{R}}_A|}\times$$

- In the following we will simply drop the "tilde" symbol and denote $\hat{T}/2E_{\mathrm{I}}$ as $\hat{T}$, $\hat{W}_{\mathrm{ee}}/2E_{\mathrm{I}}$ as $\hat{W}_{\mathrm{ee}}$, $\hat{V}_{\mathrm{ne}}/2E_{\mathrm{I}}$ as $\hat{V}_{\mathrm{ne}}$, and $\hat{H}/2E_{\mathrm{I}}$ as $\hat{H}$.

Hellmann–Feynman theorem

- Let us consider the electronic Schrödinger equation

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

where $\mathbf{Q} = (Q_1, Q_2, \ldots)$ is a collection of parameters (which, of course, does not include $\mathbf{q}$!).

- The $\mathbf{Q}$-dependent eigenvector $|\Psi(\mathbf{Q})\rangle$ is normalized for any $\mathbf{Q}$: $\boxed{\langle\Psi(\mathbf{Q})|\Psi(\mathbf{Q})\rangle = 1}$.

- The Hellmann–Feynman theorem states that $\boxed{\dfrac{\mathrm{d}E(\mathbf{Q})}{\mathrm{d}Q_i} = \left\langle \Psi(\mathbf{Q}) \middle| \dfrac{\partial \hat{H}(\mathbf{Q})}{\partial Q_i} \middle| \Psi(\mathbf{Q}) \right\rangle}$.

Proof:

$$\frac{\mathrm{d}E(\mathbf{Q})}{\mathrm{d}Q_i} = \left\langle \Psi(\mathbf{Q}) \middle| \frac{\partial \hat{H}(\mathbf{Q})}{\partial Q_i} \middle| \Psi(\mathbf{Q}) \right\rangle + \underbrace{\left\langle \frac{\partial \Psi(\mathbf{Q})}{\partial Q_i} \middle| \hat{H}(\mathbf{Q}) \middle| \Psi(\mathbf{Q}) \right\rangle + \left\langle \Psi(\mathbf{Q}) \middle| \hat{H}(\mathbf{Q}) \middle| \frac{\partial \Psi(\mathbf{Q})}{\partial Q_i} \right\rangle}_{E(\mathbf{Q}) \frac{\mathrm{d}}{\mathrm{d}Q_i}\left[\langle\Psi(\mathbf{Q})|\Psi(\mathbf{Q})\rangle\right] = 0}$$

- Application to the calculation of molecular forces: $\mathbf{Q}=\{\mathbf{R}_B\}_B \leftarrow$ position vectors of the nuclei !

The electronic Hamiltonian equals (in atomic units)

$$\hat{H}(\mathbf{Q}) \equiv \sum_{i=1}^{N} -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\times \qquad -\sum_{i=1}^{N}\sum_{B}^{\text{nuclei}}\frac{Z_B}{|\mathbf{r}_i-\mathbf{R}_B|}\times$$

thus leading to

$$\frac{\partial \hat{H}(\mathbf{Q})}{\partial \mathbf{R}_A} \equiv -\sum_{i=1}^{N}\frac{Z_A(\mathbf{r}_i-\mathbf{R}_A)}{|\mathbf{r}_i-\mathbf{R}_A|^3}\times \qquad .$$

The total energy (including nuclear-nuclear repulsions) reads

$$V(\mathbf{Q}) = E(\mathbf{Q}) + \sum_{B<C}^{\text{nuclei}}\frac{Z_B Z_C}{|\mathbf{R}_B-\mathbf{R}_C|}$$

so that, according to the Hellmann–Feynman theorem, the force applied to nucleus A equals

$$\boxed{\mathbf{F}_A(\mathbf{Q}) = -\frac{\mathrm{d}V(\mathbf{Q})}{\mathrm{d}\mathbf{R}_A} = \left\langle \Psi(\mathbf{Q}) \left| \sum_{i=1}^{N}\frac{Z_A(\mathbf{r}_i-\mathbf{R}_A)}{|\mathbf{r}_i-\mathbf{R}_A|^3}\times \right| \Psi(\mathbf{Q}) \right\rangle + \sum_{B\neq A}^{\text{nuclei}}\frac{Z_A Z_B(\mathbf{R}_A-\mathbf{R}_B)}{|\mathbf{R}_A-\mathbf{R}_B|^3}}$$

- Note that

$$\left\langle \Psi(\mathbf{Q}) \left| \overbrace{\sum_{i=1}^{N} \frac{Z_A(\mathbf{r}_i - \mathbf{R}_A)}{|\mathbf{r}_i - \mathbf{R}_A|^3} \times}^{\text{one-electron operator}} \right| \Psi(\mathbf{Q}) \right\rangle$$

$$= \int \mathrm{d}\mathbf{r}_1 \ldots \int \mathrm{d}\mathbf{r}_N \;\Psi^*(\mathbf{Q}, \mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_{i=1}^{N} \frac{Z_A(\mathbf{r}_i - \mathbf{R}_A)}{|\mathbf{r}_i - \mathbf{R}_A|^3} \times \overbrace{\Psi(\mathbf{Q}, \mathbf{r}_1, \ldots, \mathbf{r}_N)}^{\text{electronic wavefunction}}$$

$$= \sum_{i=1}^{N} \int \mathrm{d}\mathbf{r}_i \; \underbrace{(-1) \times \left[\prod_{j \neq i} \int \mathrm{d}\mathbf{r}_j \, |\Psi(\mathbf{Q}, \mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 \right]}_{\text{density of charge for electron } i \text{ at position } \mathbf{r}_i} Z_A \frac{\mathbf{R}_A - \mathbf{r}_i}{|\mathbf{r}_i - \mathbf{R}_A|^3}$$

Stationarity condition

- Let us consider a function $f : x \mapsto f(x)$ and the Taylor expansion around x_0 through first order in $\delta x = x - x_0$:

$$f(x) = f(x_0 + \delta x) = f(x_0) + \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x_0} \times \delta x \quad + \ldots$$

- We denote $\delta f(x_0)$ the expansion of $f(x_0 + \delta x) - f(x_0)$ through first order in δx:

$$\boxed{\delta f(x_0) = \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x_0} \times \delta x}.$$

- x_0 is a stationary point for f if $\boxed{\delta f(x_0) = 0}$ for any value of δx.
- In this example, where f is a function, the stationarity condition reads $\left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x_0} = 0$.
- Extrema of f (minima or maxima) are, for example, stationary points.

- Let us now consider the energy functional $E:\ \Psi \mapsto E[\Psi]=\langle\Psi|\hat{H}|\Psi\rangle$ which applies to normalized wavefunctions Ψ only.

- Note that the electronic wavefunction Ψ is a function of the electron coordinates. The energy is a "function" of Ψ,

$$E[\Psi]=\int \mathrm{d}\mathbf{r}_1 \ldots \int \mathrm{d}\mathbf{r}_N\ \Psi^*(\mathbf{r}_1,\ldots,\mathbf{r}_N)\hat{H}\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N),$$

  hence the name functional.

- The normalization condition $\langle\Psi|\Psi\rangle=1$ implies $\boxed{\langle\Psi|\hat{H}-E[\Psi]|\Psi\rangle=0}$.

- If we consider infinitesimal variations $\Psi\rightarrow\Psi+\delta\Psi$ around Ψ that preserve normalization, we have $\delta\langle\Psi|\hat{H}-E[\Psi]|\Psi\rangle=0$, thus leading to $\delta E[\Psi]=2\langle\delta\Psi|\hat{H}-E[\Psi]|\Psi\rangle$. Therefore

$$\boxed{\delta E[\Psi]=0 \quad\Leftrightarrow\quad \hat{H}|\Psi\rangle=E[\Psi]|\Psi\rangle}$$

- **Important conclusion:** both ground- and excited-state wavefunctions are stationary points for the energy functional.

Mathematical interlude: Lagrangian

- Rather than taking into account the normalization constraint $1 - \langle \Psi | \Psi \rangle = 0$ explicitly in the derivation of the stationarity condition, it is more convenient to introduce the so-called lagrangian functional (or simply Lagrangian),

$$\mathcal{L}[\Psi, \mathcal{E}] = E[\Psi] + \mathcal{E}\big(1 - \langle \Psi | \Psi \rangle\big),$$

where $\mathcal{E}$, which is referred to as Lagrange multiplier, is a number that has to be determined.

- The stationarity condition can then be rewritten as

$$\frac{\partial \mathcal{L}[\Psi, \mathcal{E}]}{\partial \mathcal{E}} = 0 \quad \rightarrow \quad 1 - \langle \Psi | \Psi \rangle = 0$$ normalization condition !

AND

$$\delta \mathcal{L}[\Psi, \mathcal{E}] = 0 \quad \rightarrow \quad 2\langle \delta\Psi | \hat{H} - \mathcal{E} | \Psi \rangle = 0$$ for any $\delta\Psi$ (no constraint)

- Note that, when Ψ is stationary, $\mathcal{E} = E[\Psi]$.

Variational principle for the excited states

- Note that the first excited-state energy E_1 can be obtained variationally under normalization ($\langle\Psi|\Psi\rangle = 1$) and orthogonality ($\langle\Psi|\Psi_0\rangle = 0$) constraints:

$$\boxed{E_1 = \min_{\Psi\perp\Psi_0} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_1|\hat{H}|\Psi_1\rangle}$$

Proof:

Since $\langle\Psi|\Psi_0\rangle = 0 = C_0, \quad |\Psi\rangle = \sum_{I>0} C_I|\Psi_I\rangle$ and

$$\langle\Psi|\hat{H}|\Psi\rangle - E_1\langle\Psi|\Psi\rangle = \sum_{I>0} C_I^2\Big(E_I - E_1\Big) \geq 0.$$

- Additional orthogonality constraints ($\langle\Psi|\Psi_1\rangle = 0$, ...) enable to reach second and higher excited-state energies.