Variational principle, stationarity condition and Hückel method

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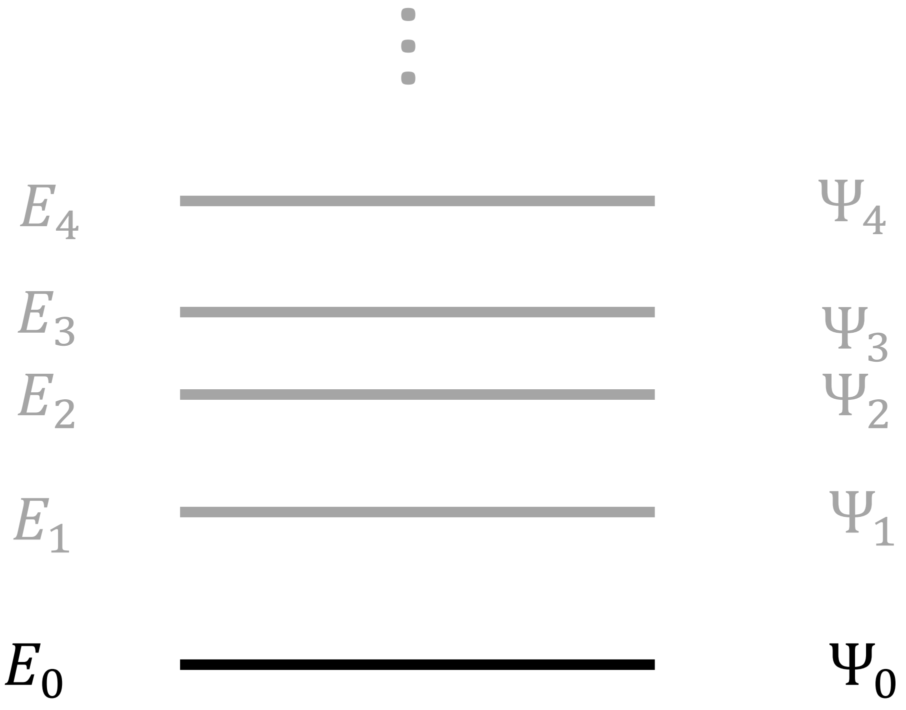
Schrödinger equation for the *ground* state

$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$



Variational principle for the ground state

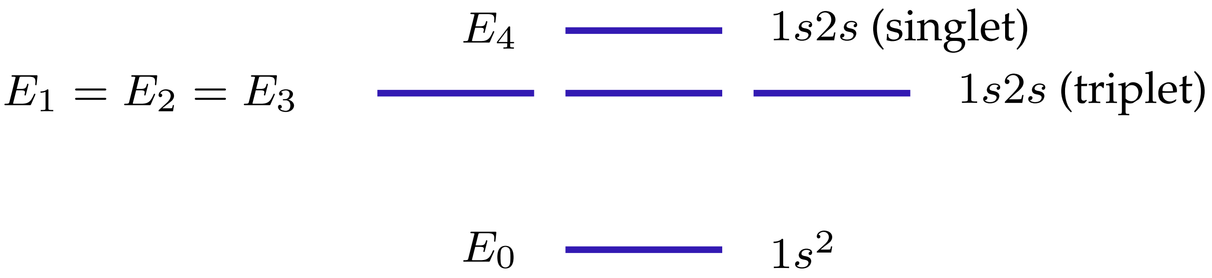
- Real algebra will be used in the following: $\langle\Psi|\Phi\rangle = \langle\Phi|\Psi\rangle^* = \langle\Phi|\Psi\rangle$.
- Let $\{|\Psi_I\rangle\}_{I=0,1,2,\ldots}$ be the orthonormal eigenstates of any Hamiltonian operator $\hat{H}$:

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

- These states are exact solutions to the time-independent Schrödinger equation.
- In the following, $|\Psi_0\rangle$ denotes the ground state i.e. the eigenstate with lowest energy. For simplicity, we will assume that the ground state is *not* degenerate:

$$E_I > E_0 \quad \text{if} \quad I > 0.$$

Example: the lowest five states of the helium atom can be represented as follows,



(Rayleigh–Ritz) variational principle for the ground state

- **Theorem**: the exact ground-state energy is a lower bound for the expectation value of the energy. The minimum is reached when the trial quantum state $|\Psi\rangle$ equals the ground state $|\Psi_0\rangle$:

$$\boxed{E_0 = \min_{\Psi} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Psi_0|\hat{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \min_{\Psi,\langle\Psi|\Psi\rangle=1} \langle\Psi|\hat{H}|\Psi\rangle.}$$

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

- In the previous description of the ground state (the so-called non variational one) we had to solve the time-independent Schrödinger equation (which is an eigenvalue equation) and select the lowest energy. In this so-called variational formulation, we "just" have to minimize the expectation value for the energy in order to determine E_0.
- The variational formulation is convenient for performing (practical) approximate calculations of ground-state wavefunctions. As discussed further in the following we can, for example, expand the trial quantum state $|\Psi\rangle$ in a finite basis of states whose dimension is much smaller than the dimension of the full space of quantum states (which can actually be infinite !).

Stationarity condition for both ground and excited states

- Let us return to the exact theory. Any trial quantum state $|\Psi\rangle$ can be decomposed as follows,

$$|\Psi\rangle = \sum_{I\geq 0} C_I|u_I\rangle. \qquad \text{We denote} \quad \mathbf{C} = \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_I \\ \vdots \end{bmatrix} \quad \text{the set of variational parameters}$$

and $\{|u_I\rangle\}_{I=0,1,\ldots}$ is an arbitrary orthonormal basis. Thus, $|\Psi\rangle$ becomes a function of $\mathbf{C}$, hence the notation $|\Psi(\mathbf{C})\rangle$ used in the following.

- Consequently, the trial energy $\Big[$i.e. the expectation value of the energy obtained for $|\Psi(\mathbf{C})\rangle\Big]$ is also a function of $\mathbf{C}$:

$$E(\mathbf{C}) = \frac{\langle\Psi(\mathbf{C})|\hat{H}|\Psi(\mathbf{C})\rangle}{\langle\Psi(\mathbf{C})|\Psi(\mathbf{C})\rangle} = \frac{\displaystyle\sum_{I\geq 0, J\geq 0} C_I C_J \langle u_I|\hat{H}|u_J\rangle}{\displaystyle\sum_{I\geq 0} C_I^2}.$$

Stationarity condition for both ground and excited states

- **Theorem**: $|\Psi(\mathbf{C})\rangle$ is an eigenstate of $\hat{H}$ if and only if it fulfills the following stationarity condition,

$$\boxed{\frac{\partial E(\mathbf{C})}{\partial C_J} = 0, \quad \forall J \geq 0.}$$

Proof:

$$\frac{\partial}{\partial C_J}\Big(\langle\Psi(\mathbf{C})|\Psi(\mathbf{C})\rangle E(\mathbf{C})\Big) = \frac{\partial}{\partial C_J}\Big(\langle\Psi(\mathbf{C})|\hat{H}|\Psi(\mathbf{C})\rangle\Big)$$

$$\longrightarrow \quad 2E(\mathbf{C})\Big\langle\frac{\partial\Psi(\mathbf{C})}{\partial C_J}\Big|\Psi(\mathbf{C})\Big\rangle + \langle\Psi(\mathbf{C})|\Psi(\mathbf{C})\rangle\frac{\partial E(\mathbf{C})}{\partial C_J} = 2\Big\langle\frac{\partial\Psi(\mathbf{C})}{\partial C_J}\Big|\hat{H}\Big|\Psi(\mathbf{C})\Big\rangle$$

where $\Big|\frac{\partial\Psi(\mathbf{C})}{\partial C_J}\Big\rangle = |u_J\rangle.$ Therefore, using the resolution of the identity leads to

$$\begin{aligned}\hat{H}|\Psi(\mathbf{C})\rangle - E(\mathbf{C})|\Psi(\mathbf{C})\rangle &= \sum_{J\geq 0}\Big(\langle u_J|\hat{H}|\Psi(\mathbf{C})\rangle - E(\mathbf{C})\langle u_J|\Psi(\mathbf{C})\rangle\Big)|u_J\rangle \\ &= \frac{1}{2}\langle\Psi(\mathbf{C})|\Psi(\mathbf{C})\rangle\sum_{J\geq 0}\frac{\partial E(\mathbf{C})}{\partial C_J}|u_J\rangle.\end{aligned}$$

Stationarity condition for both ground and excited states

- Note that the stationarity condition applies not only to the ground state but also to the excited states.

- However, excited states do not minimize locally the expectation value of the energy.

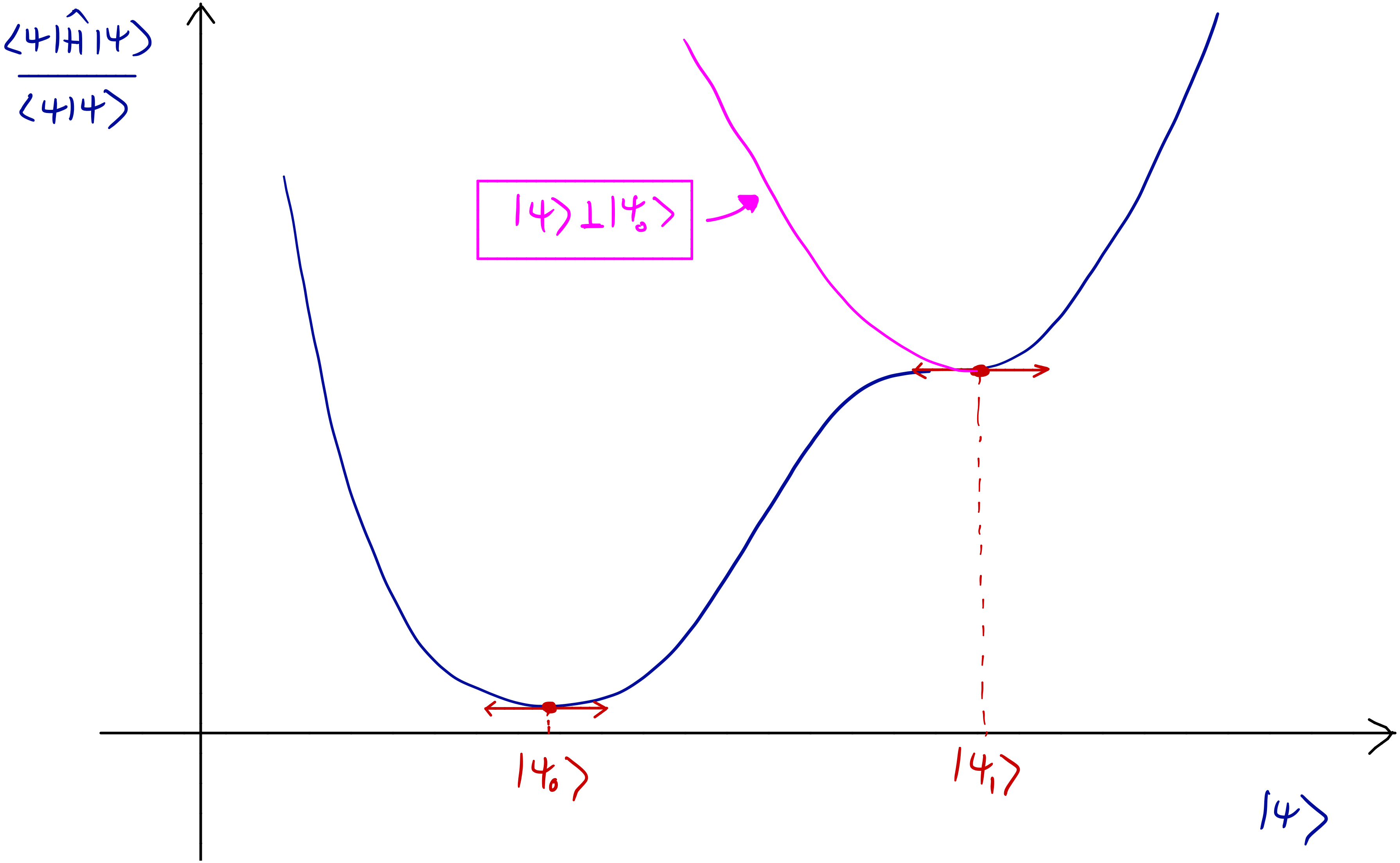
- This can be easily illustrated by considering the trial quantum state $|\Psi(\xi)\rangle = \xi|\Psi_0\rangle + |\Psi_1\rangle$

  and the corresponding trial energy $E(\xi) = \dfrac{\langle\Psi(\xi)|\hat{H}|\Psi(\xi)\rangle}{\langle\Psi(\xi)|\Psi(\xi)\rangle}$ which are both functions of ξ.

  We then see that

  $$E(\xi) - E_1 = \frac{\xi^2 E_0 + E_1}{\xi^2 + 1} - E_1 = \frac{\xi^2}{\xi^2 + 1}\big(E_0 - E_1\big) < 0 \quad \text{when } \xi \text{ deviates from } 0.$$

Stationarity condition for both ground and excited states



From the exact theory to approximate methods

- There exists for some (simple) systems like the hydrogen atom exact analytical solutions to the Schrödinger equation.

- There are no analytical solutions to the electronic Schrödinger equation for atoms or molecules with more than one electron.

- Therefore, in order to apply quantum mechanics to chemistry or solid state physics, we need a strategy for approaching numerically (i.e. with a computer) the exact solutions.

- Of course we should check that, in case an exact analytical solution exists, the latter (or a solution close to it) is recovered with such a strategy.

From the exact theory to approximate methods

- Let us consider the example of the hydrogen atom. The exact $1s$ orbital, which is obtained by solving the Schrödinger equation in an infinite dimension space of quantum states, reads in atomic units $\left[\text{i.e.}\quad \mathbf{r} \leftarrow \mathbf{r}/a_0 \equiv (x/a_0, y/a_0, z/a_0)\right]$,

$$\Psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\, e^{-r} \qquad \text{where} \qquad r = |\mathbf{r}|.$$

- In standard quantum chemistry codes, Gaussian functions are used instead of the above (so-called Slater) function: for example, $\Phi_1(\mathbf{r}) = e^{-2.23r^2}$, $\Phi_2(\mathbf{r}) = e^{-0.41r^2}$ or $\Phi_3(\mathbf{r}) = e^{-0.11r^2}$.

- We would like to approach the exact solution with a linear combination of these three functions:

$$\Psi_0(\mathbf{r}) \approx \tilde{\Psi}_0(\mathbf{r}) = \tilde{C}_1\ \Phi_1(\mathbf{r}) + \tilde{C}_2\ \Phi_2(\mathbf{r}) + \tilde{C}_3\ \Phi_3(\mathbf{r}).$$

A simple but non trivial question is: how to determine the "best" coefficients $\tilde{C}_1$, $\tilde{C}_2$ and $\tilde{C}_3$?

From the exact theory to approximate methods

- Let us consider a second example: the H_2^+ molecule.

  The exact ground-state molecular orbital $\Psi_0(\mathbf{r})$ can *a priori* be approximated by the linear combination of the $1s$ atomic orbitals that are centered on the (fixed) hydrogen atoms located at positions $\mathbf{R}_A$ and $\mathbf{R}_B$, respectively. In this case, we use only two basis functions:

$$\Psi_0(\mathbf{r}) \approx \tilde{\Psi}_0(\mathbf{r}) = \tilde{C}_1\ \Phi_1(\mathbf{r}) + \tilde{C}_2\ \Phi_2(\mathbf{r}),$$

  where $\Phi_1(\mathbf{r}) = \dfrac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$ and $\Phi_2(\mathbf{r}) = \dfrac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_B|}$.

  How can we determine the "best" values for $\tilde{C}_1$ and $\tilde{C}_2$?

Comment: the atomic orbitals Φ_1 and Φ_2 are not necessarily orthogonal:

$$\langle \Phi_1 | \Phi_2 \rangle = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\ \Phi_1^*(\mathbf{r})\Phi_2(\mathbf{r}) = \frac{1}{\pi}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\ e^{-|\mathbf{r}-\mathbf{R}_A|} \times e^{-|\mathbf{r}-\mathbf{R}_B|} = S_{12} \qquad \longleftarrow \quad \text{overlap integral}$$

S_{12} equals zero in the dissociation limit $\big(|\mathbf{R}_A - \mathbf{R}_B| \rightarrow +\infty\big)$.

Variational approximate method: general formulation

- Let us consider a subspace $\mathcal{E}_M$ of the full space of quantum states. The integer M denotes the (finite) dimension of $\mathcal{E}_M$ and $\{|\Phi_I\rangle\}_{I=1,2,\ldots,M}$ is a (not necessarily orthonormal) basis of that subspace.

- Let us build the so-called overlap matrix (also referred to as metric matrix) as follows,

$$S = \begin{bmatrix} \langle\Phi_1|\Phi_1\rangle & \langle\Phi_1|\Phi_2\rangle & \ldots & \langle\Phi_1|\Phi_M\rangle \\ \langle\Phi_2|\Phi_1\rangle & \langle\Phi_2|\Phi_2\rangle & \ldots & \langle\Phi_2|\Phi_M\rangle \\ \vdots & \vdots & \vdots & \vdots \\ \langle\Phi_M|\Phi_1\rangle & \langle\Phi_M|\Phi_2\rangle & \ldots & \langle\Phi_M|\Phi_M\rangle \end{bmatrix}.$$

  Moreover, we introduce the so-called Hamiltonian matrix:

$$H = \begin{bmatrix} \langle\Phi_1|\hat{H}|\Phi_1\rangle & \langle\Phi_1|\hat{H}|\Phi_2\rangle & \ldots & \langle\Phi_1|\hat{H}|\Phi_M\rangle \\ \langle\Phi_2|\hat{H}|\Phi_1\rangle & \langle\Phi_2|\hat{H}|\Phi_2\rangle & \ldots & \langle\Phi_2|\hat{H}|\Phi_M\rangle \\ \vdots & \vdots & \vdots & \vdots \\ \langle\Phi_M|\hat{H}|\Phi_1\rangle & \langle\Phi_M|\hat{H}|\Phi_2\rangle & \ldots & \langle\Phi_M|\hat{H}|\Phi_M\rangle \end{bmatrix}.$$

- In this context the trial quantum state reads

$$|\Psi(\tilde{\mathbf{C}})\rangle = \sum_{I=1}^{M} \tilde{C}_I |\Phi_I\rangle \qquad \text{where} \qquad \tilde{\mathbf{C}} = \begin{bmatrix} \tilde{C}_1 \\ \tilde{C}_2 \\ \vdots \\ \tilde{C}_M \end{bmatrix} \qquad \longleftarrow \quad \text{variational parameters}$$

- The trial energy can be written in terms of the Hamiltonian and metric matrices as follows,

$$E(\tilde{\mathbf{C}}) = \frac{\langle \Psi(\tilde{\mathbf{C}})|\hat{H}|\Psi(\tilde{\mathbf{C}})\rangle}{\langle \Psi(\tilde{\mathbf{C}})|\Psi(\tilde{\mathbf{C}})\rangle} = \frac{\displaystyle\sum_{I,J=1}^{M} \tilde{C}_I \tilde{C}_J H_{IJ}}{\displaystyle\sum_{I,J=1}^{M} \tilde{C}_I \tilde{C}_J S_{IJ}}.$$

- It can be shown that the stationarity condition $\dfrac{\partial E(\tilde{\mathbf{C}})}{\partial \tilde{C}_J} = 0, \quad \forall J = 1, M$ is equivalent, in this context, to

$$\boxed{H\tilde{\mathbf{C}} = E(\tilde{\mathbf{C}})S\tilde{\mathbf{C}}} \qquad \longleftarrow$$ **approximate** calculation of the ground and **some** excited states.

Comment : if the basis of the subspace $\mathcal{E}_M$ is orthonormal (i.e. $S = [\hat{\mathbb{1}}]$), we obtain the eigenvalue equation $H\tilde{\mathbf{C}} = E(\tilde{\mathbf{C}})\tilde{\mathbf{C}}$ which is nothing but the time-independent Schrödinger equation projected onto $\mathcal{E}_M$.

- An energy $\tilde{E}$ is solution if there exists a non-zero column vector $\tilde{\mathbf{C}}$ such that

  $$\left(H - \tilde{E}S\right)\tilde{\mathbf{C}} = 0,$$

  which implies that the so-called secular determinant is equal to zero,

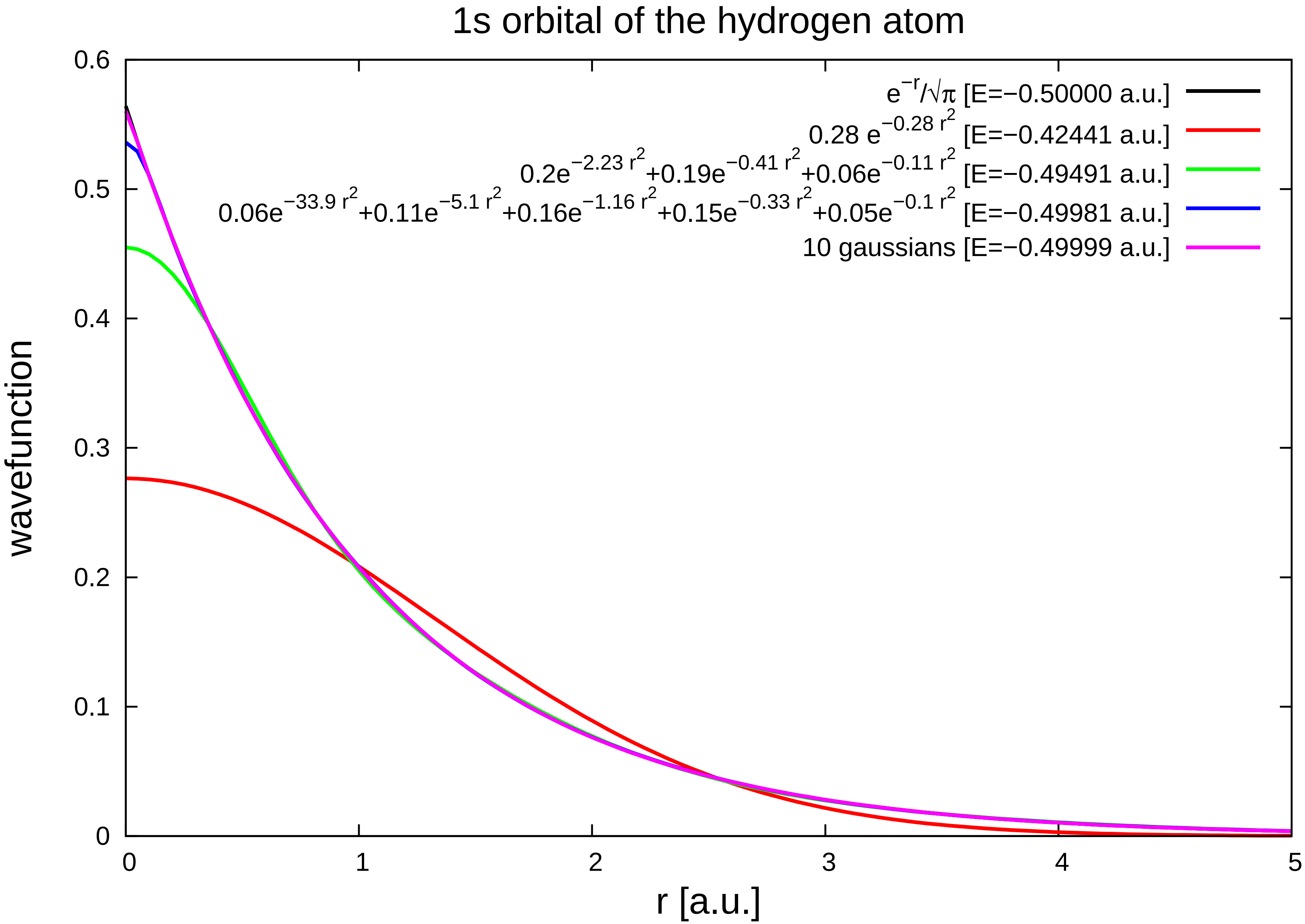
  $$\boxed{\det\left(H - \tilde{E}S\right) = 0}$$

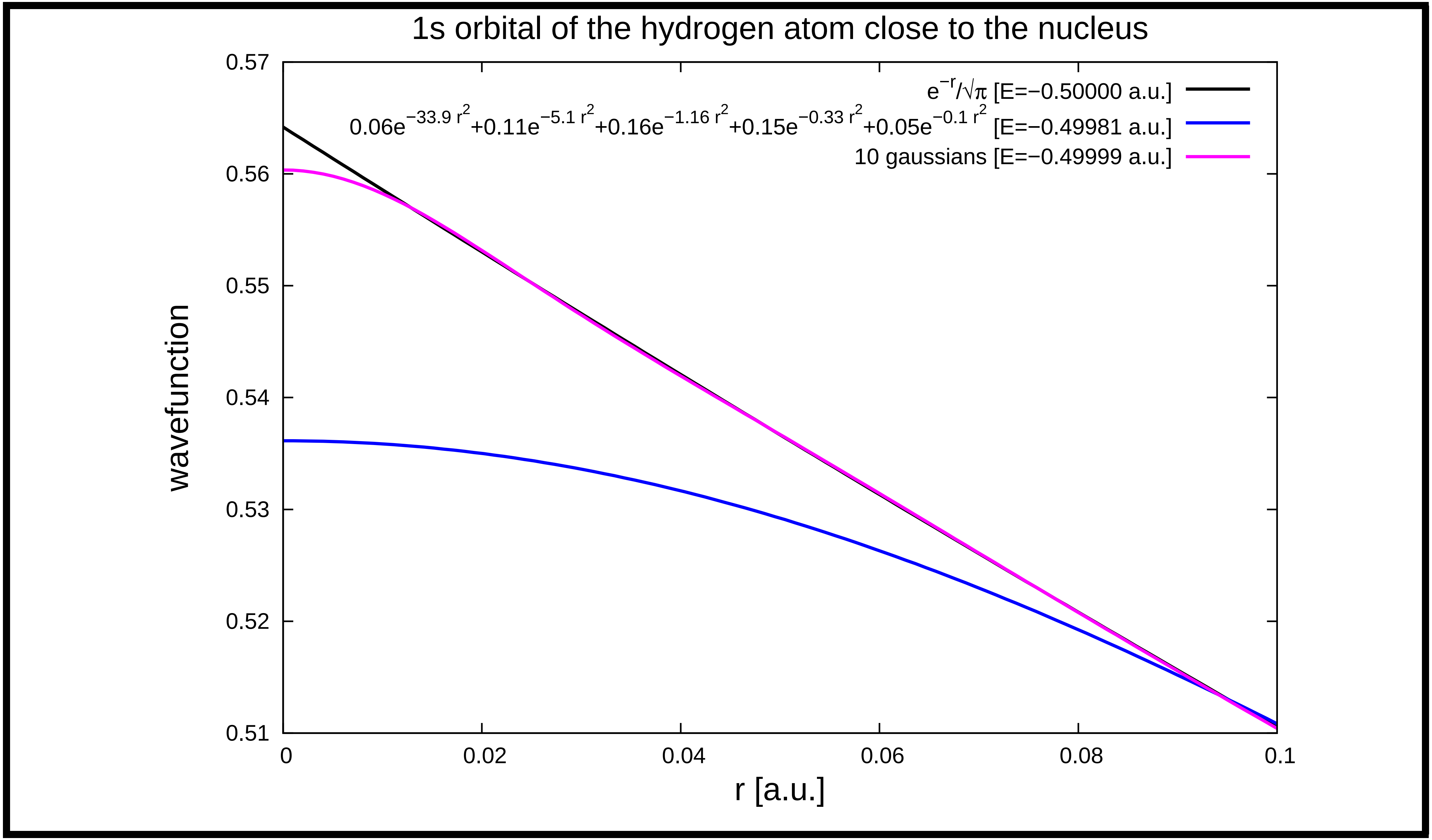
  since $\left(H - \tilde{E}S\right)$ cannot be inverted.

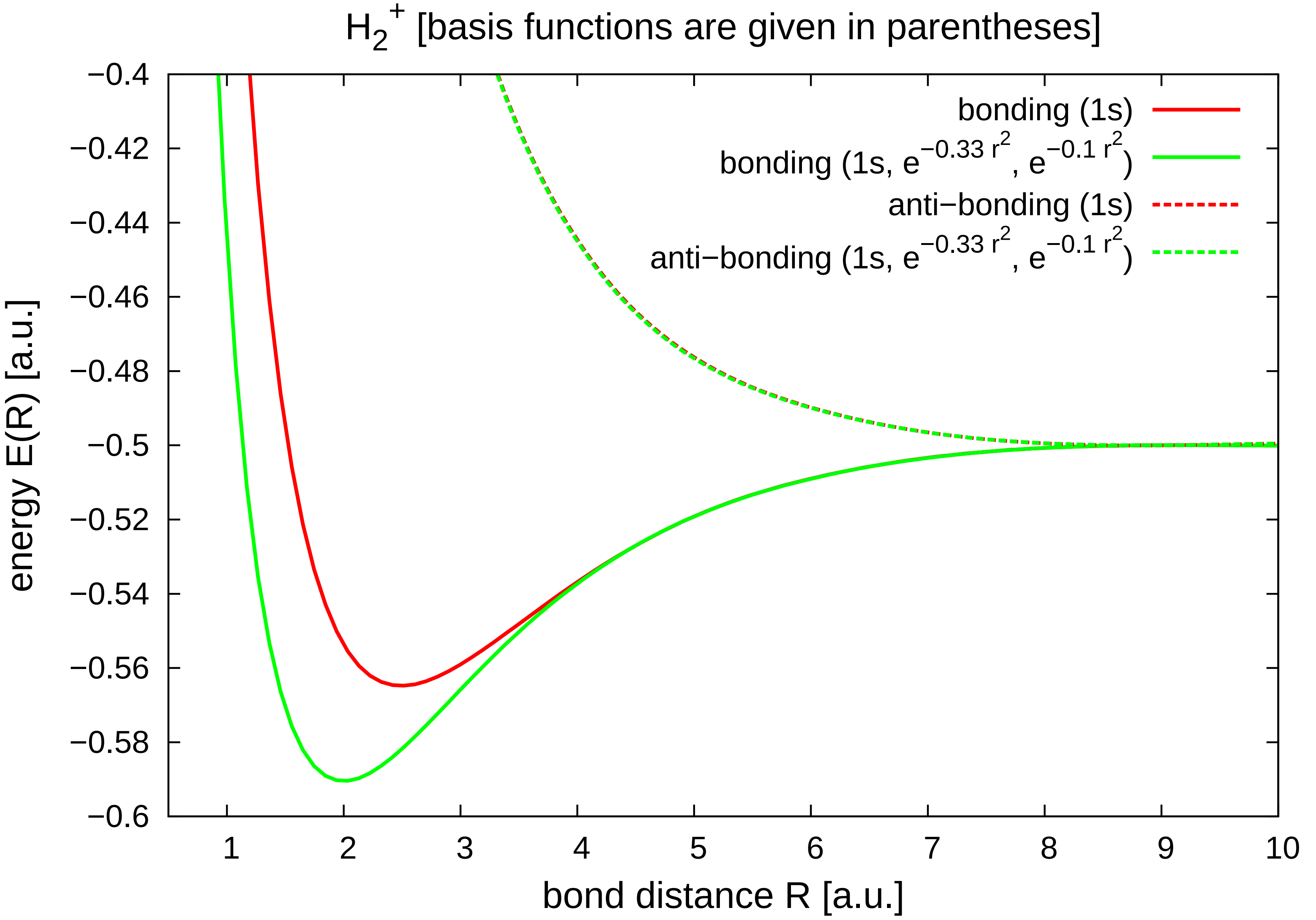
- Application to the hydrogen atom: $\hat{H} \equiv -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{e^2}{4\pi\varepsilon_0 r}\times$

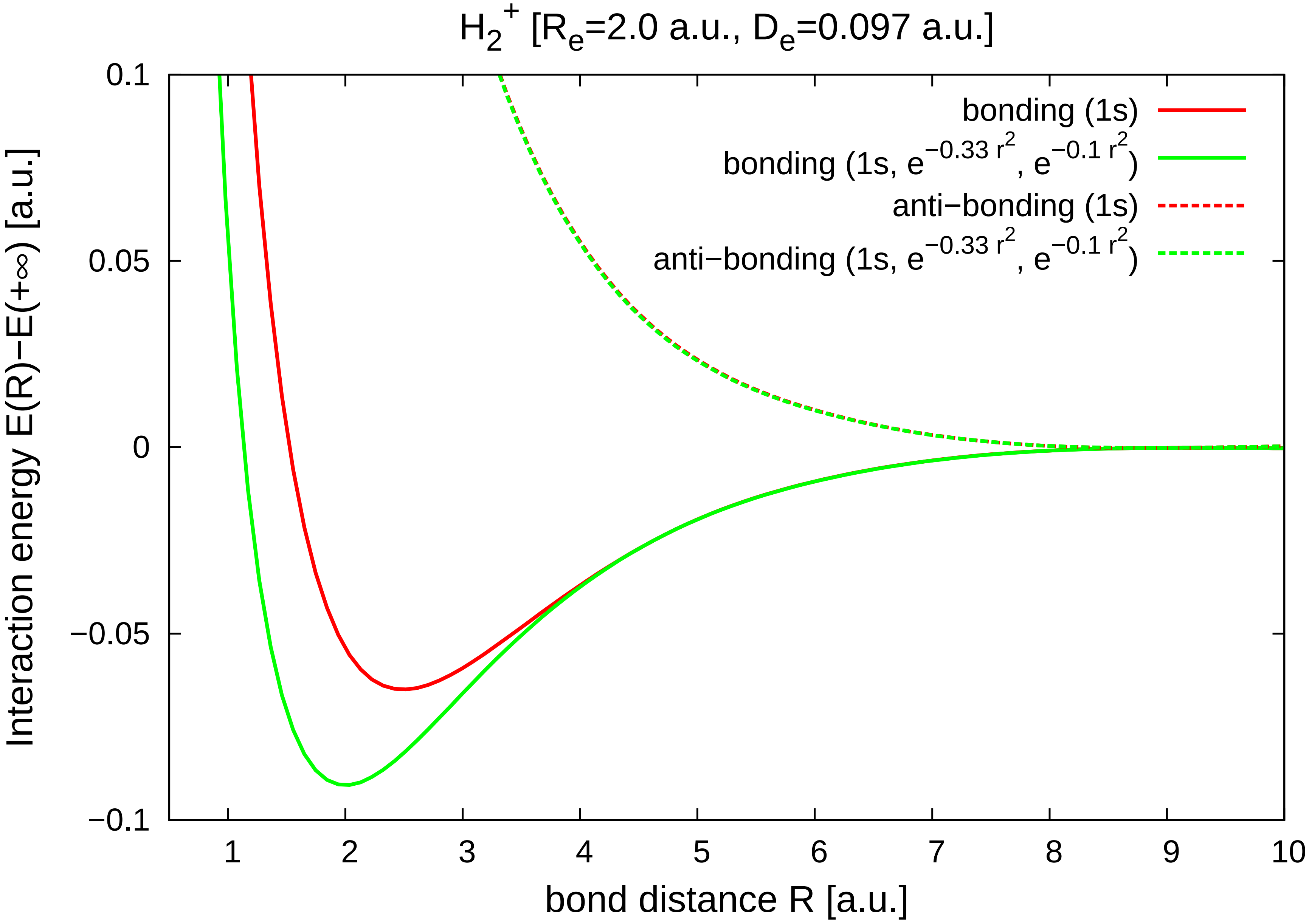
- Application to the H_2^+ molecule: in this case the Hamiltonian operator reads

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{|\mathbf{r}-\mathbf{R}_A|} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|} + \frac{1}{|\mathbf{R}_A-\mathbf{R}_B|}\right)\times$$


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
wavefunction
r [a.u.]
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
$e^{-r}/\sqrt{\pi}$ [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.]


H_2^+ [basis functions are given in parentheses]
bonding (1s)
bonding (1s, $e^{-0.33\,r^2}$, $e^{-0.1\,r^2}$)
anti−bonding (1s)
anti−bonding (1s, $e^{-0.33\,r^2}$, $e^{-0.1\,r^2}$)
energy E(R) [a.u.]
−0.4
−0.42
−0.44
−0.46
−0.48
−0.5
−0.52
−0.54
−0.56
−0.58
−0.6
1
2
3
4
5
6
7
8
9
10
bond distance R [a.u.]


H_2^+ [R_e=2.0 a.u., D_e=0.097 a.u.]
Interaction energy E(R)−E(+∞) [a.u.]
bond distance R [a.u.]
0.1
0.05
0
−0.05
−0.1
1
2
3
4
5
6
7
8
9
10
bonding (1s)
bonding (1s, $e^{-0.33 r^2}$, $e^{-0.1 r^2}$)
anti−bonding (1s)
anti−bonding (1s, $e^{-0.33 r^2}$, $e^{-0.1 r^2}$)

Many-electron systems

- If we want to apply the approximate variational method introduced previously to a system that contains more than one electron like, for example, the hydrogen molecule, then we need basis functions Φ_I that describe two electrons $\Big(\Phi_I \equiv \Phi_I(\mathbf{r}_1, \mathbf{r}_2)\Big)$ and we must use the following two-electron Hamiltonian:

$$\begin{aligned}\hat{H} \quad \equiv \quad & -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_2} + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|}\right) \times \\ & + \frac{e^2}{4\pi\varepsilon_0}\left(\underbrace{\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}}_{\text{two-electron repulsion}} + \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|}\right) \times\end{aligned}$$

- In the following we will consider a much simpler approximation (referred to as one-electron approximation) which consists in **(i)** defining a Hamiltonian operator $\hat{h}$ for one electron, **(ii)** applying the variational method to it and, finally, **(iii)** distributing the electrons among the calculated molecular orbitals. The many-electron energy is then obtained by summing up the energies of the occupied (spin-) orbitals.
- In the Hückel method, the overlap between atomic orbitals is neglected when the variational method is applied $\big(S \approx [\hat{\mathbb{1}}]\big)$.

The Hückel method applied to H_2

- We choose as atomic orbitals the $1s$ orbitals centered on each hydrogen atom in order to apply the variational method: $\Phi_1(\mathbf{r}) = \dfrac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$ and $\Phi_2(\mathbf{r}) = \dfrac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_B|}$.
- Construction of the Hamiltonian matrix:

$$\langle \Phi_1|\hat{h}|\Phi_1\rangle = \langle \Phi_2|\hat{h}|\Phi_2\rangle = \alpha \quad \longleftarrow \quad \text{for symmetry reasons}$$

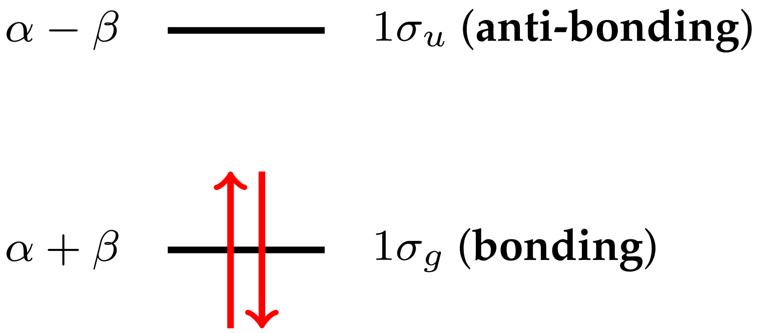
$$\langle \Phi_1|\hat{h}|\Phi_2\rangle = \langle \Phi_2|\hat{h}|\Phi_1\rangle = \beta$$

- No numerical values for α and β are actually needed for giving a qualitative description of the bond between the two atoms. We just need to impose the condition $\beta < 0$ (this will be discussed later on).
- Consequently, the secular determinant reads $\begin{vmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{vmatrix} = (\alpha - \varepsilon)^2 - \beta^2 = 0$

$$\rightarrow \quad \varepsilon_{1\sigma_g} = \alpha + \beta \quad \text{and} \quad \varepsilon_{1\sigma_u} = \alpha - \beta.$$

- The corresponding normalized molecular orbitals are $\Phi_{1\sigma_g}(\mathbf{r}) = \dfrac{1}{\sqrt{2}}\Big(\Phi_1(\mathbf{r}) + \Phi_2(\mathbf{r})\Big)$ and $\Phi_{1\sigma_u}(\mathbf{r}) = \dfrac{1}{\sqrt{2}}\Big(\Phi_1(\mathbf{r}) - \Phi_2(\mathbf{r})\Big)$.

The Hückel method applied to H_2



$\alpha - \beta$ $1\sigma_u$ **(anti-bonding)**

$\alpha + \beta$ $1\sigma_g$ **(bonding)**

- The ground-state electronic configuration of H_2 is denoted $\left(1\sigma_g\right)^2$.

- The total electronic energy equals $2(\alpha + \beta)$.

- The bond order ($B.O.$) is defined as follows,

$$B.O. = \frac{\text{number of electrons in } \textbf{bonding} \text{ orbitals } - \text{number of electrons in } \textbf{anti-bonding} \text{ orbitals}}{2}$$

Here $B.O. = 1 \longrightarrow$ single bond :-)

- Similarly, we would obtain $B.O. = (2-2)/2 = 0$ for the helium dimer (no covalent bond !).