The simplest molecule H_2^+

H_2^+ is the simplest of all molecules comprising of two protons bind together by a single electron. With in Born-Oppenheimer approximation, the Hamiltonian operator for this molecule, in atomic units, is given by

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R},$$

where r_A and r_B are distances of the electron from nuclei A and B, while R is the internuclear separation. In the above formula, the last term on the right side, $1/R$, corresponds to the repulsion energy between the two protons. To calculate the ground state electronic energy of this molecule, we can use the variational theorem. To begin with, let us expand the ground state (i.e., bonding molecular orbital) as the linear combination

$$\psi_{\text{bond}} = c_1 1s_A + c_2 1s_B$$

where, by symmetry, $c_1 = c_2 = 1/\sqrt{2}$, while $1s_A$ and $1s_B$ are hydrogen atomic orbitals centered on nuclei A and B. The energy is computed as the expectation value

$$E_{\text{bond}} = \frac{\int d\tau \ \psi_{\text{bond}}^* \hat{H} \psi_{\text{bond}}}{\int d\tau \ \psi_{\text{bond}}^* \psi_{\text{bond}}},$$

where the integration is typically performed in elliptical coordinates:

$$\int d\tau = \frac{R^3}{8} \int_1^\infty du \int_{-1}^1 dv \int_0^{2\pi} d\phi \quad u^2 - v^2$$

After plugging in the function $1s_X = \sqrt{\zeta^3/\pi} \exp\left(-\zeta r_X\right)$ (where $X = A$, B), and some manipulations, the expression for energy simplifies to

$$E_{\text{bond}} = \frac{J + K}{1 + S} + \frac{1}{R},$$

where $J(\zeta, R) = \zeta^2/2 - \zeta - 1/R + (\zeta + 1/R)\exp(-2\zeta R)$, $K(\zeta, R) = -\zeta^2 S(\zeta, R)/2 - \zeta(1 + \zeta R)(2 - \zeta)\exp(-\zeta R)$, and finally $S(\zeta, R) = (1 + \zeta R + (\zeta R)^2/3)\exp(-\zeta R)$. Now the optimal value of ζ and R can be computed by a two-dimensional minimization of the function $E_{\text{bond}}(\zeta, R)$. The corresponding energy at the optimal value of ζ and R is the electronic energy of H_2^+. If the energy of a H atom is subtracted from E_{bond} one arrives at the bond energy ΔE_{bond}.

1. Report ζ_{opt}, R_{opt}, ΔE_{bond} and compare these values with their exact non-relativistic counterparts, $R_{\text{opt}}^{\text{exact}} = 105.69$ pm and $\Delta E_{\text{bond}}^{\text{exact}} = -0.1026$ hartree.

2. For various fixed values of R in the range 1.0 to 10 bohr, minimize E_{bond} by optimizing ζ. Plot the resulting ΔE_{bond} as a function of R. Explain the features of this plot.