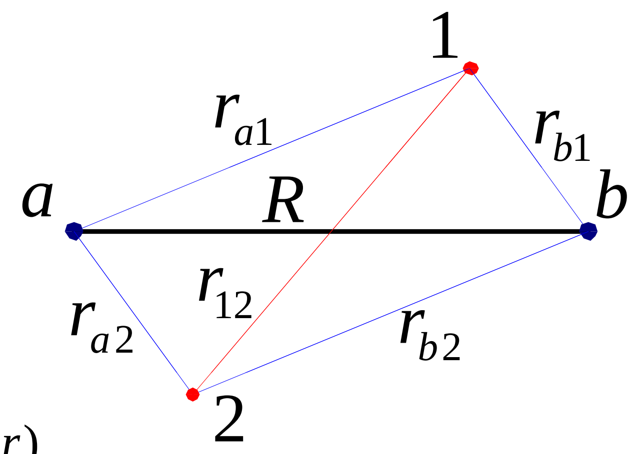
Heitler – London method

for H_2 molecule



$$E(R) = \min_r E_{\mathrm{HL}}(r,R), \qquad E_{\mathrm{HL}}(r,R) = \frac{\langle \Psi_r | H | \Psi_r \rangle}{\langle \Psi_r | \Psi_r \rangle}$$

$$\Psi_r(\vec{r}_1, \vec{r}_2) = \exp(-r_{a1}/r)\exp(-r_{b2}/r) + \exp(-r_{b1}/r)\exp(-r_{a2}/r)$$

$$E_{\mathrm{HL}}(r,R) = T_{\mathrm{HL}}(r,R) + V_{\mathrm{HL}}^{(1)}(r,R) + V_{\mathrm{HL}}^{(2)}(r,R) + \frac{1}{R}$$

- $T_{\mathrm{HL}}(r,R)$ ↑ electron kinetic energy
- $V_{\mathrm{HL}}^{(1)}(r,R)$ ↑ interaction between electrons and nuclei
- $V_{\mathrm{HL}}^{(2)}(r,R)$ ↑ interaction between electrons $\left\langle \frac{1}{r_{12}} \right\rangle$

$$T_{\mathrm{HL}}(r,R) = \frac{9\left(1+e^{\frac{2R}{r}}\right)r^4 + 18Rr^3 + 9R^2r^2 - R^4}{9e^{\frac{2R}{r}}r^6 + (3r^2+3Rr+R^2)^2 r^2} \qquad V_{\mathrm{HL}}^{(1)}(r,R) = -\frac{6(r+R)\left[3\left(-1+e^{\frac{2R}{r}}\right)r^3 + 6Rr^2 + 6R^2r + 2R^3\right]}{R\left[9e^{\frac{2R}{r}}r^4 + (3r^2+3Rr+R^2)^2\right]}$$

$$\begin{aligned} V_{\mathrm{HL}}^{(2)}(r,R) = {} & 3\left[12\left(-5+5e^{\frac{2R}{r}}+6\gamma\right)r^4 + 9(-5+16\gamma)Rr^3 + 6(-19+20\gamma)R^2r^2\right. \\ & + 2(-23+24\gamma)R^3r + 4(-1+2\gamma)R^4 + 8e^{\frac{4R}{r}}\left(3r^2-3Rr+R^2\right)^2 \mathrm{Ei}\left(-\frac{4R}{r}\right) \\ & \left. - 16e^{\frac{2R}{r}}\left(9r^4-3R^2r^2+R^4\right)\mathrm{Ei}\left(-\frac{2R}{r}\right) + 8\left(3r^2+3Rr+R^2\right)^2 \log\left(\frac{R}{r}\right)\right] \\ & \times \left\{20R\left[9e^{\frac{2R}{r}}r^4 + \left(3r^2+3Rr+R^2\right)^2\right]\right\}^{-1}. \end{aligned}$$

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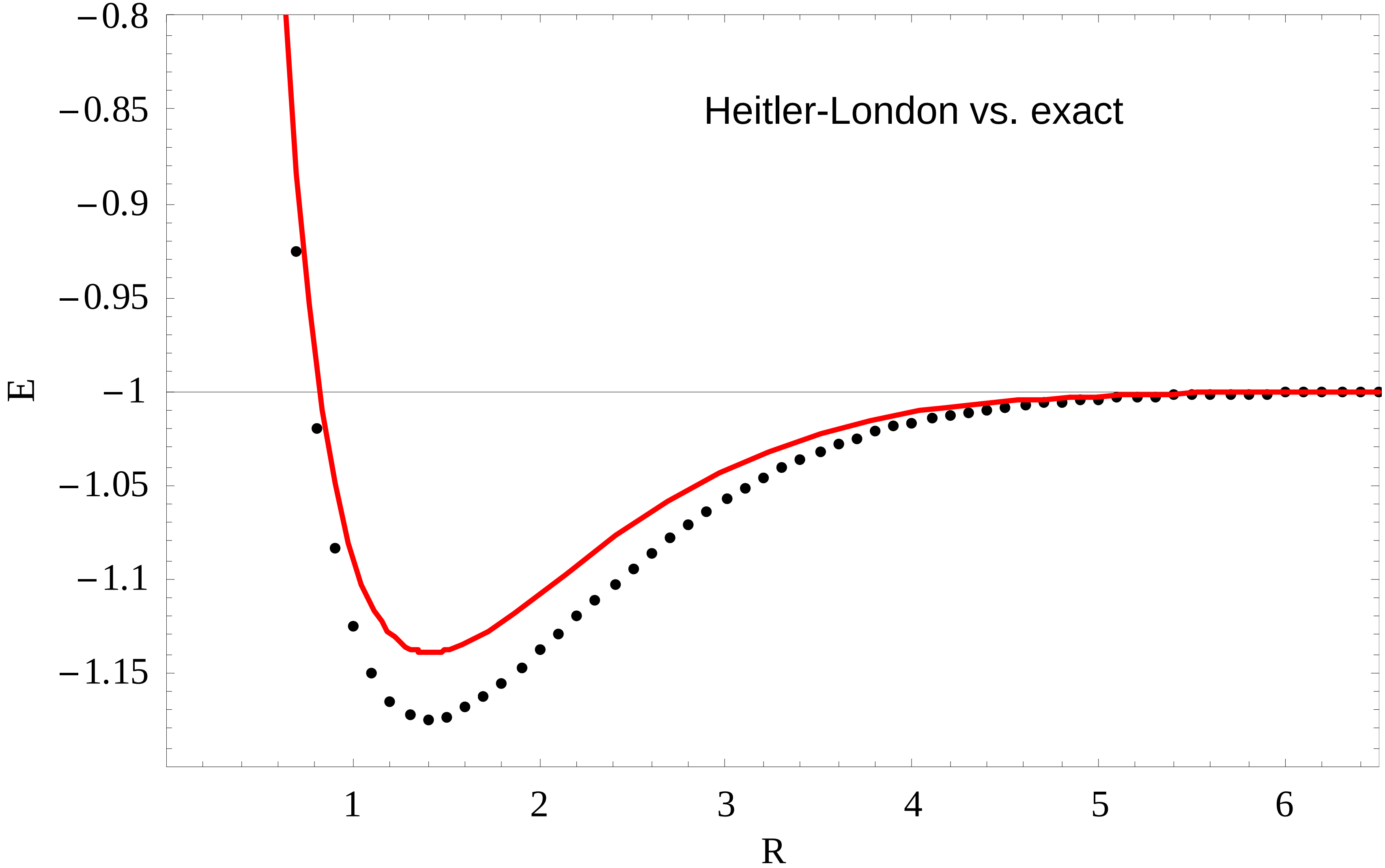
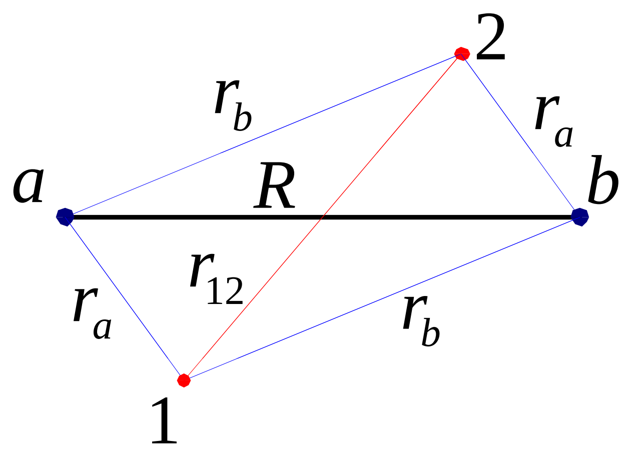

Heitler-London vs. exact
E
R
−0.8
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
1
2
3
4
5
6

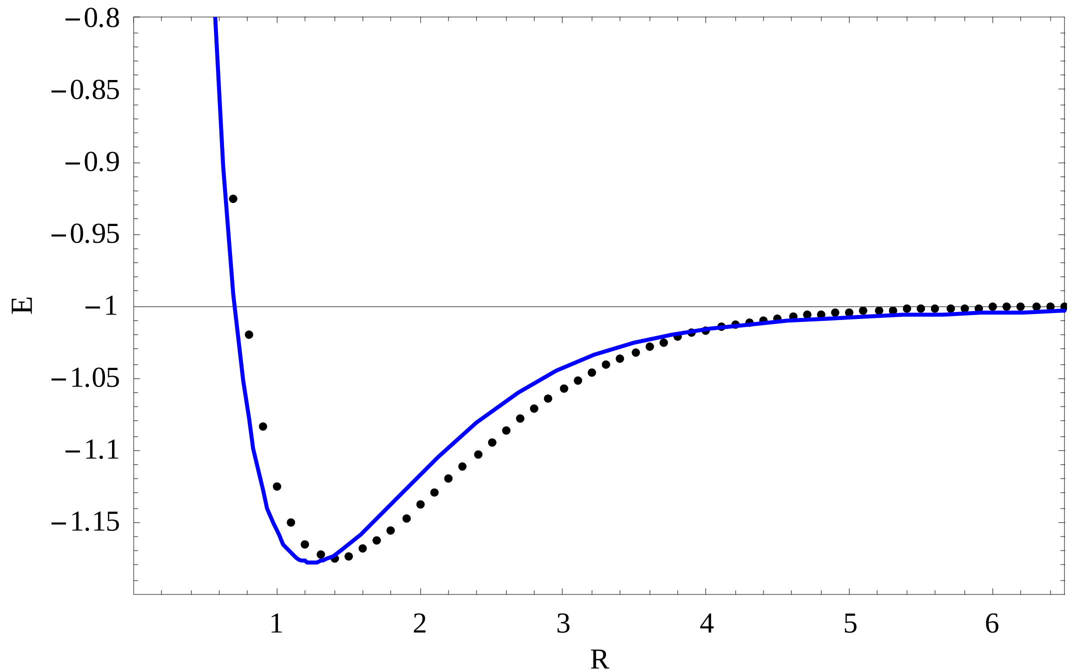
Hybrid HL-B model



$$E(r_a, R) = T_{\mathrm{HL}}(r_a, R) + V_{\mathrm{HL}}^{(1)}(r_a, R) + \frac{1}{r_{12}} + \frac{1}{R}$$

Constraint

$$T_{\mathrm{HL}}(r_a, R) + V_{\mathrm{HL}}^{(1)}(r_a, R) = \left(\frac{1}{2r_a^2} - \frac{1}{r_a} - \frac{1}{r_b} \right) \times 2$$



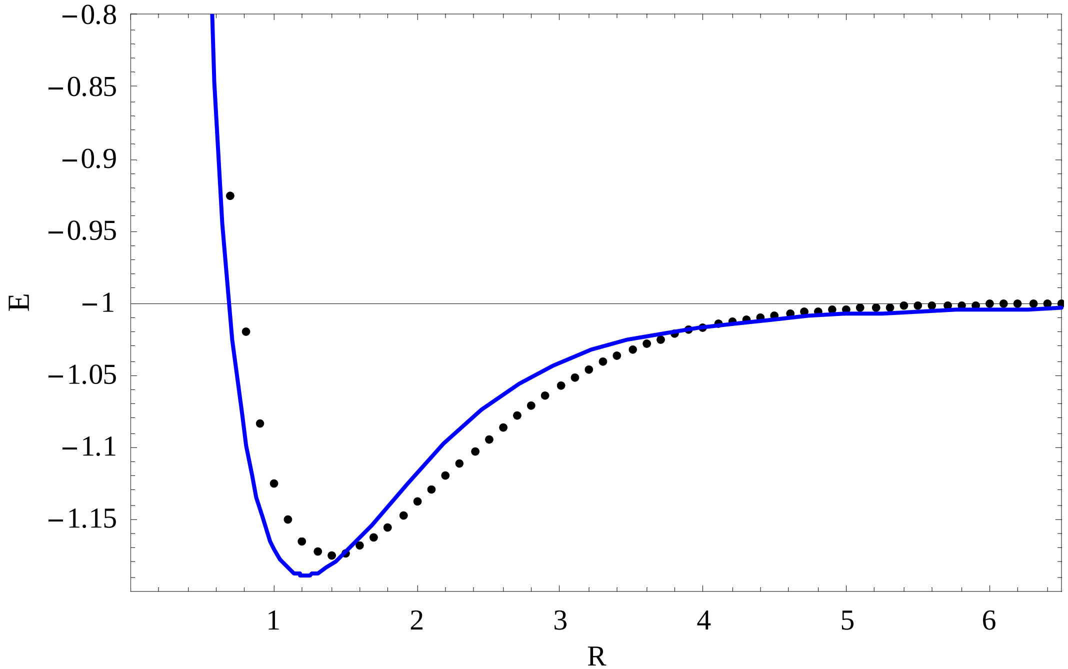
Alternative constraint

$$-\frac{1}{r_b} = \Phi(r_a, R)$$

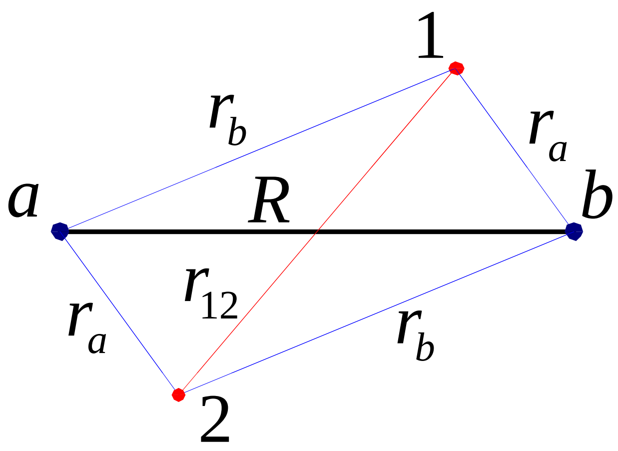
$$\Phi(r,R) = -\frac{1}{1+S^2(R/r)}\left[f(r,R) + S(R/r)g(r,R)\right]$$

$$f(r,R) = \frac{1}{R} - e^{-2R/r}\left(\frac{1}{r}+\frac{1}{R}\right),$$

$$g(r,R) = \frac{1}{r}e^{-R/r}\left(1+\frac{R}{r}\right).$$



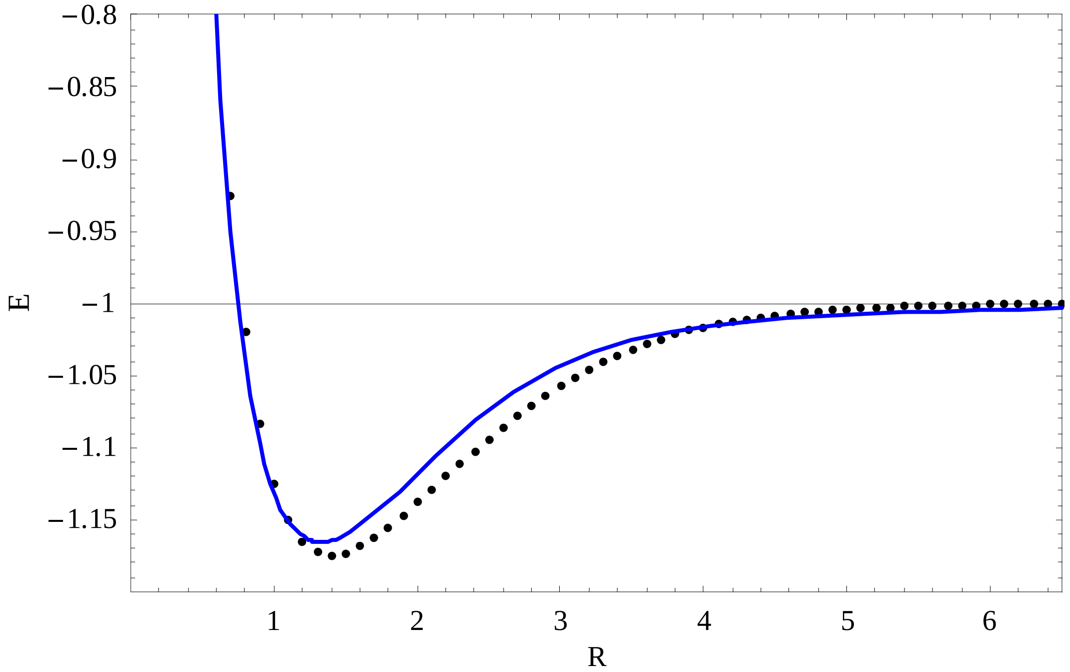
The model of Phys. Lett. A

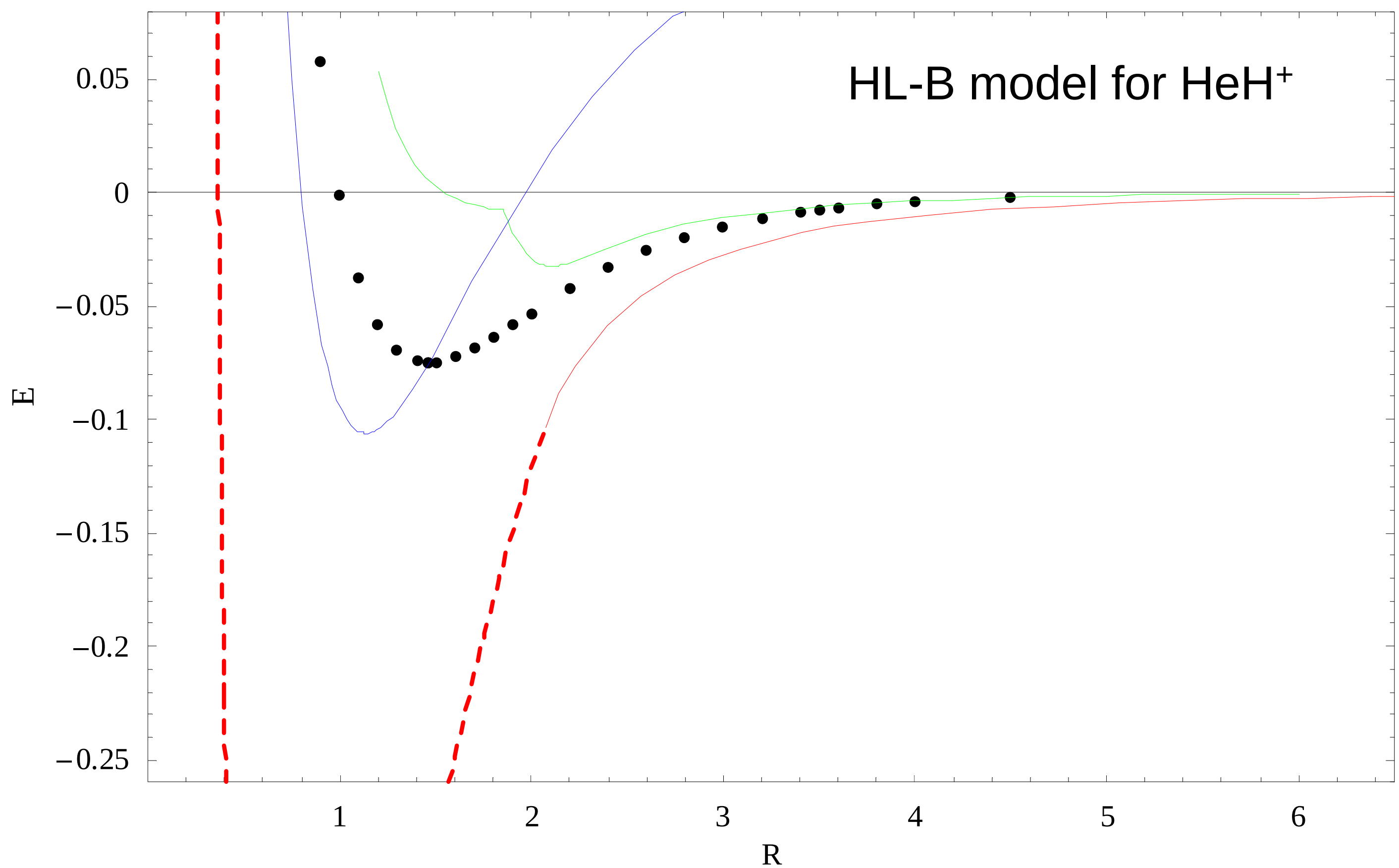


$$W(r_a, R) = \left(\frac{1}{2r_a^2} - \frac{1}{r_a} - \frac{1}{r_b} \right) \times 2 + \frac{1}{r_{12}} + \frac{1}{R}$$

Constraint

$$-\frac{1}{r_b} = \Phi(r_a, R)$$




HL-B model for HeH+
0.05
0
−0.05
−0.1
−0.15
−0.2
−0.25
E
1
2
3
4
5
6
R