Heitler - London model with Gaussian orbitals

I. GAUSSIAN ORBITAL

Defined as

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{8\bar{r}^3}} \exp\left(-\frac{\pi r^2}{8\bar{r}^2}\right), \tag{1}$$

where $\bar{r}$ is a parameter. The bar ($^-$) is added to distinguish the parameter $\bar{r}$ from the radius vector r.

The function $\phi(\boldsymbol{r})$ is normalized so that

$$\int d\boldsymbol{r}\, \phi^2(\boldsymbol{r}) = 1. \tag{2}$$

Scaling in equation (1) is chosen so that

$$\int d\boldsymbol{r}\, r^{-1}\phi^2(\boldsymbol{r}) = \bar{r}^{-1}. \tag{3}$$

Integral of the kinetic energy is

$$\int d\boldsymbol{r}\, \phi(\boldsymbol{r}) \left(-\frac{\boldsymbol{\nabla}^2}{2}\right) \phi(\boldsymbol{r}) = \frac{3\pi}{16\bar{r}^2} = \frac{1.178}{2\,\bar{r}^2}. \tag{4}$$

Other expectation values are

$$\int d\boldsymbol{r}\, r\phi^2(\boldsymbol{r}) = \frac{4}{\pi}\bar{r}, \quad \int d\boldsymbol{r}\, r^2\phi^2(\boldsymbol{r}) = \frac{6}{\pi}\bar{r}^2, \quad \int d\boldsymbol{r}\, r^{-2}\phi^2(\boldsymbol{r}) = \frac{\pi}{2}\bar{r}^{-2}. \tag{5}$$

For comparison, Slater orbital is defined as

$$\phi_{\text{Slater}}(\boldsymbol{r}) = \frac{1}{\sqrt{\pi\bar{r}^3}} \exp\left(-\frac{r}{\bar{r}}\right). \tag{6}$$

Slater and Gaussian orbitals for the same value of the parameter $\bar{r} = 1$ are plotted on Figure 1.

While equations (2) and (3) hold for the Gaussian orbital, the kinetic energy is $\frac{1}{2\bar{r}^2}$ that is slightly different from that of Gaussian orbital, equation (4). Other expectation values are different too,

$$\int d\boldsymbol{r}\, r\phi^2_{\text{Slater}}(\boldsymbol{r}) = \frac{3}{2}\bar{r}, \quad \int d\boldsymbol{r}\, r^2\phi^2_{\text{Slater}}(\boldsymbol{r}) = 3\bar{r}^2, \quad \int d\boldsymbol{r}\, r^{-2}\phi^2_{\text{Slater}}(\boldsymbol{r}) = 2\bar{r}^{-2}. \tag{7}$$

Expectation values of the operator r^n for Slater and Gaussian orbitals are plotted on Figure 2.

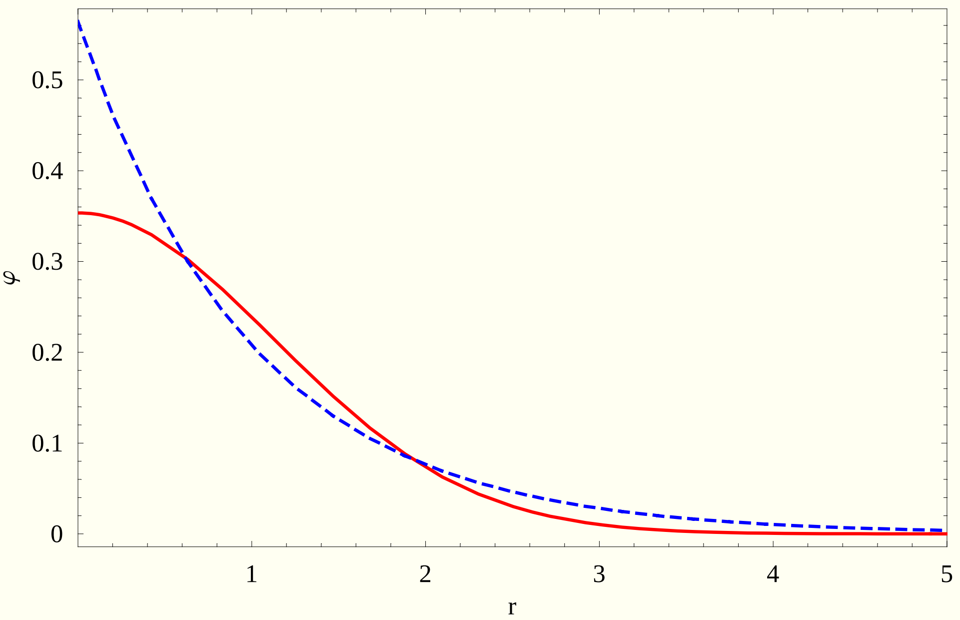

FIG. 1. A Slater orbital (solid line) and a Gaussian orbital (dashed line) for the same value of $\bar{r} = 1$.

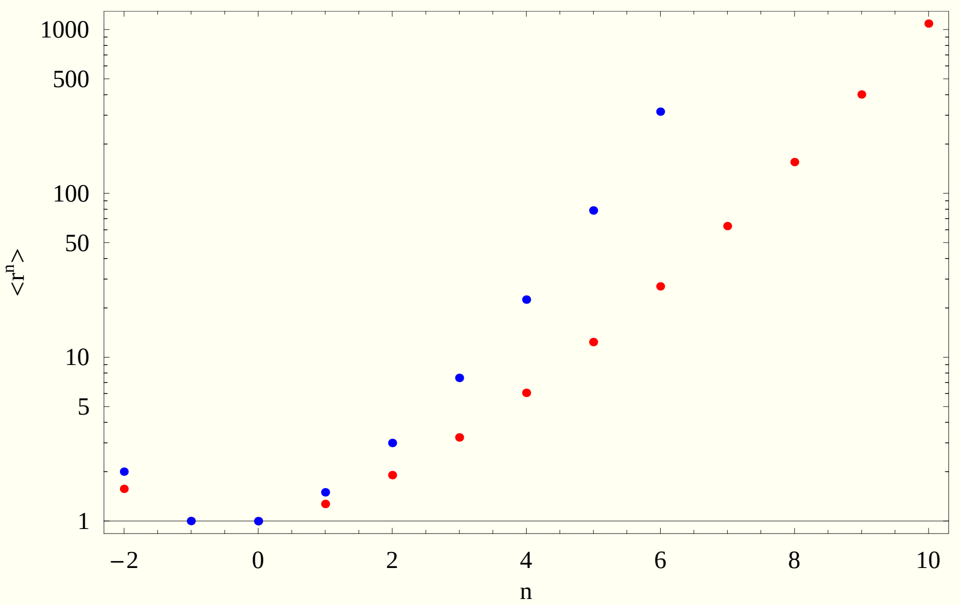

FIG. 2. Expectation values $\langle r^n \rangle$ for a Slater orbital (red dots) and a Gaussian orbital (blue dots) for the same value of $\bar{r} = 1$. For comparison, $\langle r^n \rangle = \bar{r}^n$ for the Bohr model delta-function orbital (horizontal line).

II. HEITLER - LONDON MODEL

A trial variational function is

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2(1+S^2)}} \left[\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) + \phi_a(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_1)\right], \tag{8}$$

where

$$\phi_a(\boldsymbol{r}) = \phi(\boldsymbol{r} - \boldsymbol{R}_a), \quad \phi_b(\boldsymbol{r}) = \phi(\boldsymbol{r} - \boldsymbol{R}_b), \quad |\boldsymbol{R}_a - \boldsymbol{R}_b| = R, \tag{9}$$

and the overlap integral is

$$S = \int d\boldsymbol{r}\, \phi_a(\boldsymbol{r})\phi_b(\boldsymbol{r}) = \exp\left(-\frac{\pi}{16}\frac{R^2}{\bar{r}^2}\right) = 1 - 0.196\frac{R^2}{\bar{r}^2} + 0.019\frac{R^4}{\bar{r}^4} + \ldots. \tag{10}$$

The probability density

$$P(\boldsymbol{r}_1) = \int d\boldsymbol{r}_2\, \Psi^2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2(1+S^2)} \left[\phi_a^2(\boldsymbol{r}_1) + 2S\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1) + \phi_b^2(\boldsymbol{r}_1)\right] \tag{11}$$

is plotted on Figures 3, 4.

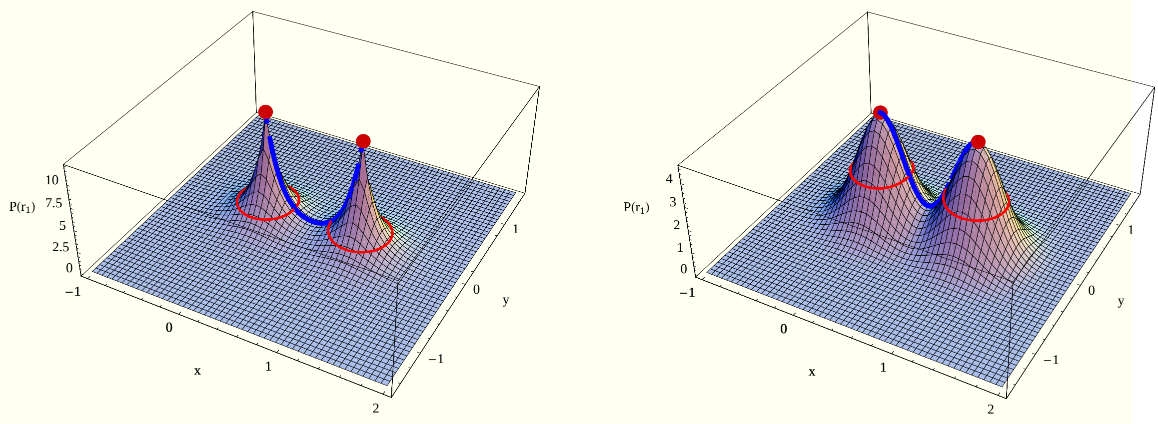

FIG. 3. Probability density plot for $R = 1$ and $\bar{r} = 0.3$. Slater wave function is to the left, and Gaussian function to the right.

In comparison,

$$S_{\text{Slater}} = \exp\left(-\frac{R}{\bar{r}}\right)\left(1 + \frac{R}{\bar{r}} + \frac{1}{3}\frac{R^2}{\bar{r}^2}\right) = 1 - 0.167\frac{R^2}{\bar{r}^2} + 0.042\frac{R^4}{\bar{r}^4} + \ldots. \tag{12}$$

The overlap integral as a function of R is plotted on Figure 5.

III. COULOMB INTEGRALS

$$f = \left\langle \phi_a \left| \frac{1}{r_b} \right| \phi_a \right\rangle = \frac{1}{R}\text{Erf}\left(\frac{\sqrt{\pi}}{2}\frac{R}{\bar{r}}\right) = \frac{1}{\bar{r}} - 0.262\frac{R^2}{\bar{r}^3} + 0.062\frac{R^4}{\bar{r}^5} + \ldots, \tag{13}$$

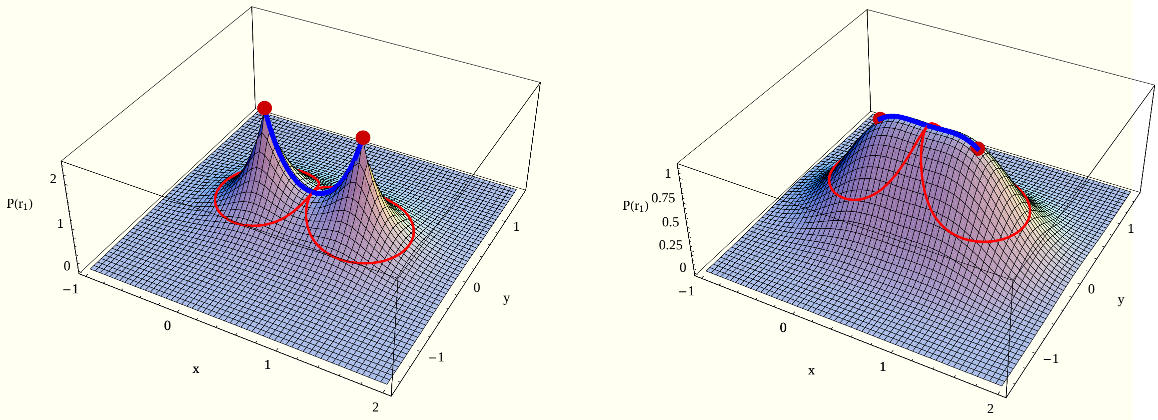

FIG. 4. Probability density plot for $R = 1$ and $\bar{r} = 0.5$. Slater wave function is to the left, and Gaussian function to the right.

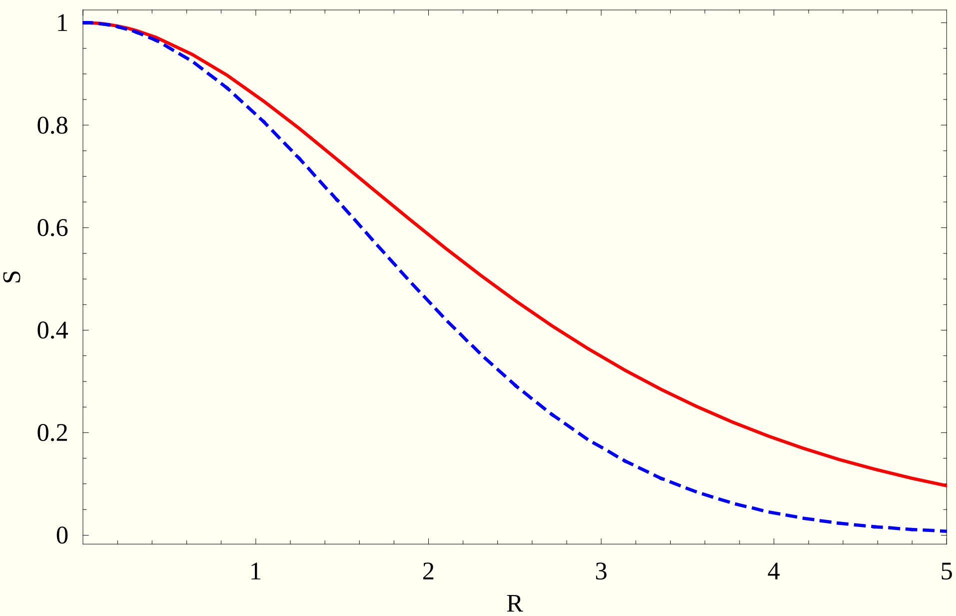

FIG. 5. Overlap integral as a function of separation distance R for a Slater orbital (solid line) and a Gaussian orbital (dashed line) for the same value of $\bar{r} = 1$.

$$g = \left\langle \phi_a \left| \frac{1}{r_b} \right| \phi_b \right\rangle = \frac{2S}{R} \mathrm{Erf}\left(\frac{\sqrt{\pi}}{4} \frac{R}{\bar{r}} \right) = \frac{1}{\bar{r}} - 0.262 \frac{R^2}{\bar{r}^3} + 0.036 \frac{R^4}{\bar{r}^5} + \ldots . \tag{14}$$

In comparison,

$$f_{\text{Slater}} = \frac{1}{R} - \exp\left(-\frac{2R}{\bar{r}} \right) \left(\frac{1}{R} + \frac{1}{\bar{r}} \right) = \frac{1}{\bar{r}} - 0.667 \frac{R^2}{\bar{r}^3} + 0.667 \frac{R^3}{\bar{r}^4} + \ldots , \tag{15}$$

$$g_{\text{Slater}} = \frac{1}{r} \exp\left(-\frac{R}{\bar{r}} \right) \left(1 + \frac{R}{\bar{r}} \right) = \frac{1}{\bar{r}} - 0.5 \frac{R^2}{\bar{r}^3} + 0.333 \frac{R^3}{\bar{r}^4} + \ldots . \tag{16}$$

The function f for Slater and Gaussian orbitals is plotted on Figure 6. The function g for Slater and Gaussian orbitals is plotted on Figure 7.

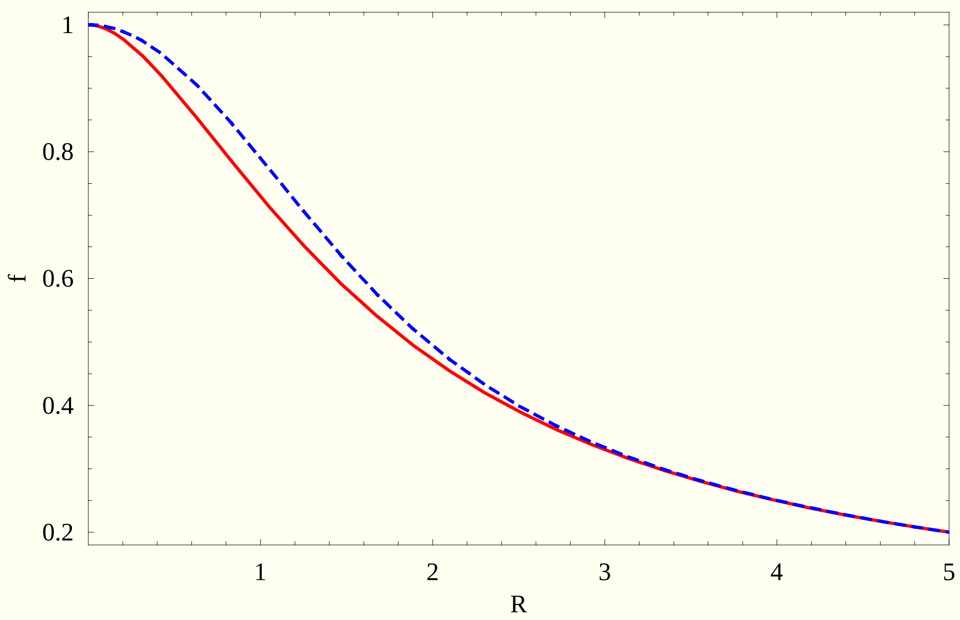

FIG. 6. The function f for a Slater orbital (solid line) and a Gaussian orbital (dashed line) for the same value of $\bar{r} = 1$.

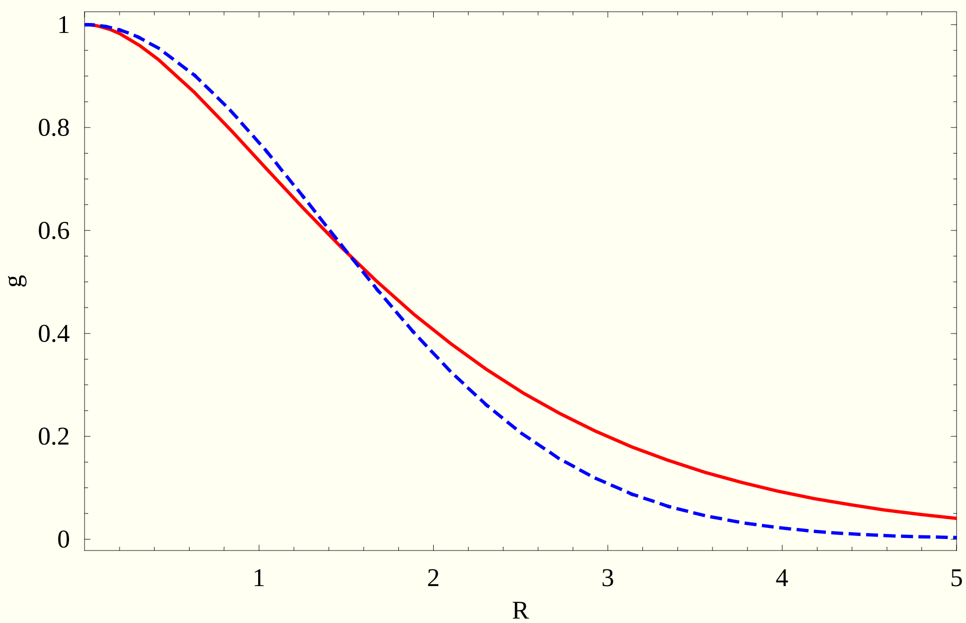

FIG. 7. The function g for a Slater orbital (solid line) and a Gaussian orbital (dashed line) for the same value of $\bar{r} = 1$.

IV. BOHR MODEL WITH A CONSTRAINT

A constraint is defined through a function $\Phi(\bar{r}, R)$ according to equation (8) from the paper in Phys. Lett. A (2006):

$$\Phi(\bar{r}, R) = \frac{f + Sg}{1 + S^2} \tag{17}$$

for Heitler - London model or as

$$\Phi(\bar{r}, R) = \frac{f + g}{1 + S} \tag{18}$$

for Hund - Mulliken model.

The energy is calculated according to a recipe of the paper in Phys. Lett. A (2006) as

$$E(R) = \min_{x,y>0} \epsilon(x, y, R) \tag{19}$$

under a constraint

$$-\frac{1}{r_b} = \Phi(r_a, R), \tag{20}$$

where

$$\epsilon(x, y, R) = \frac{1}{r_a^2} - \frac{2}{r_a} - \frac{2}{r_b} + \frac{1}{r_{12}} + \frac{1}{R}, \tag{21}$$

$$r_a = \left(x^2 + y^2\right)^{1/2}, \tag{22}$$

$$r_b = \left[(x - R)^2 + y^2\right]^{1/2}, \tag{23}$$

$$r_{12} = \left[(2x - R)^2 + 4y^2\right]^{1/2}. \tag{24}$$

Result of calculation of energy are shown on Figures 8, 9 for HL and HM models respectively.

V. HYBRID HL - BOHR MODEL

The energy is determined as

$$E_{\mathrm{HL-B}}(R) = \min_{x,y>0} \epsilon_{\mathrm{HL-B}}(x, y, R) \tag{25}$$

under a constraint

$$E_{\mathrm{B}}^{(1)} = E_{\mathrm{HL}}^{(1)}, \tag{26}$$

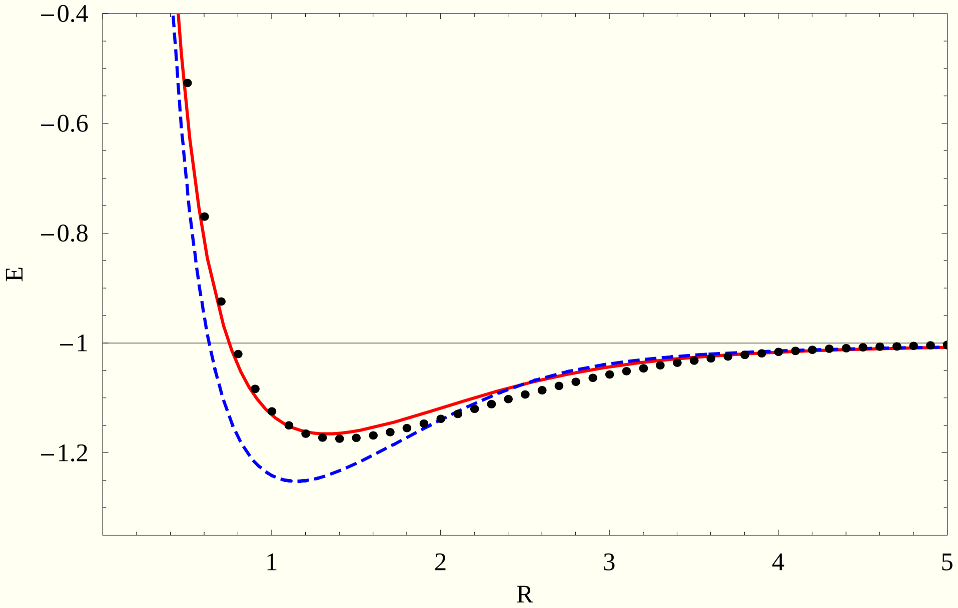

FIG. 8. Energy calculated within Heitler - London model. Solid line is based on Slater orbitals, and dashed line is based on Gaussian orbitals. Dotted line is exact energy.

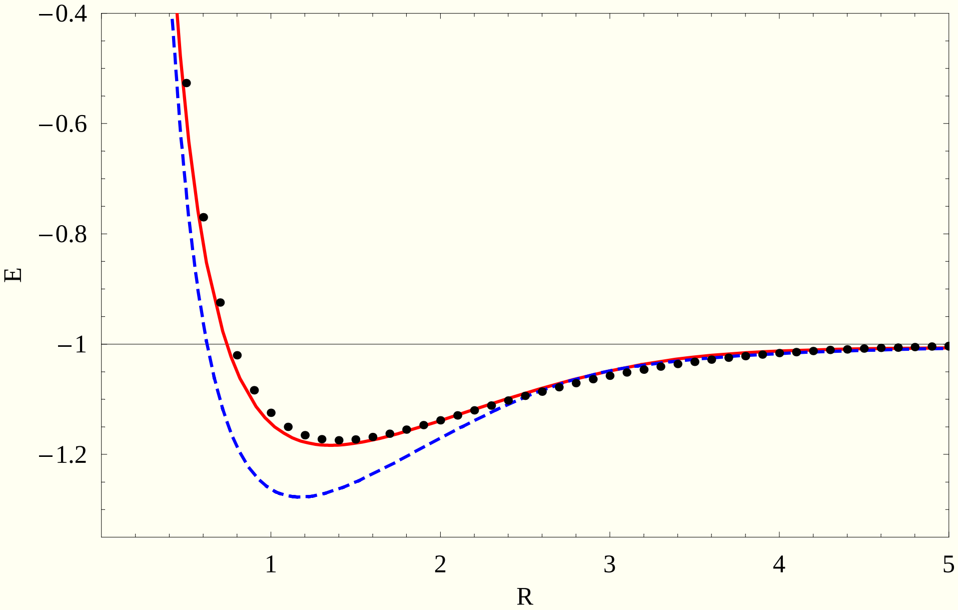

FIG. 9. Energy calculated within Hund - Mulliken model. Solid line is based on Slater orbitals, and dashed line is based on Gaussian orbitals. Dotted line is exact energy.

where

$$\epsilon_{\mathrm{HL-B}}(x,y,R) = E^{(1)}_{\mathrm{HL}} + \frac{1}{r_{12}} + \frac{1}{R}, \tag{27}$$

$$E^{(1)}_{\mathrm{B}} = \frac{1}{r_a^2} - \frac{2}{r_a} - \frac{2}{r_b}, \tag{28}$$

$$E^{(1)}_{\mathrm{HL}} = T + V_1, \tag{29}$$

$$V_1 = -\frac{2}{1+S^2}\left(\frac{1}{\bar{r}} + f + 2Sg\right), \tag{30}$$

$$T_{\mathrm{Gauss}} = \frac{3\pi}{8\bar{r}^2} - \frac{\pi^2 R^2}{64\bar{r}^4\left(1+S^2\right)}, \tag{31}$$

$$T_{\mathrm{Slater}} = \frac{9\bar{r}^4\left(1+e^{2R/\bar{r}}\right) + 18\bar{r}^3 R + 9\bar{r}^2 R^2 - R^4}{9\bar{r}^6 e^{2R/\bar{r}} + \bar{r}^2\left(3\bar{r}^2 + 3\bar{r}R + R^2\right)^2}, \tag{32}$$

$$r_a = \bar{r} = \left(x^2+y^2\right)^{1/2}, \tag{33}$$

$$r_b = \left[(x-R)^2 + y^2\right]^{1/2}, \tag{34}$$

$$r_{12} = \left[(2x-R)^2 + 4y^2\right]^{1/2}. \tag{35}$$

Result of calculation of energy are shown on Figure 10. At infinite separation, Gaussian

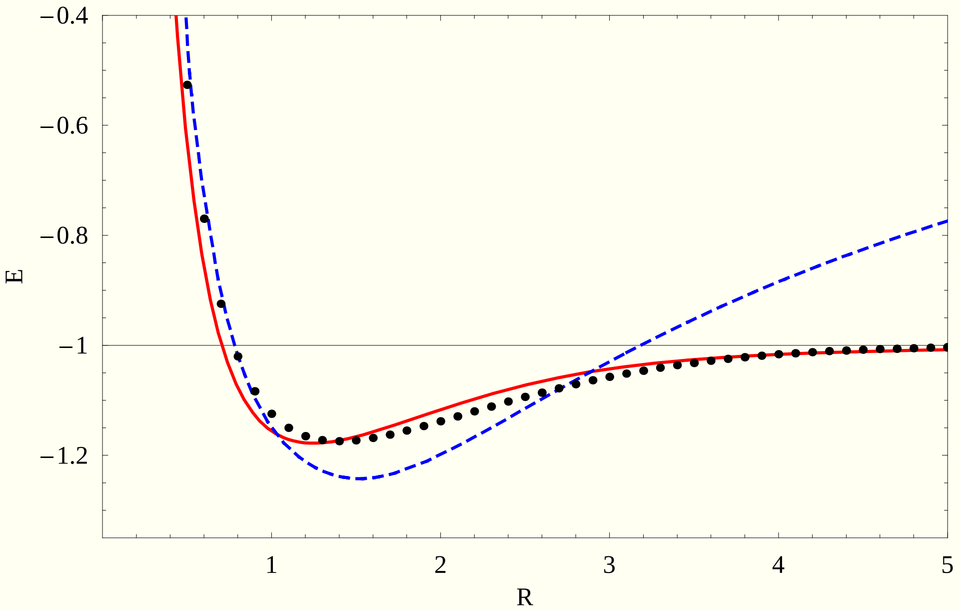

FIG. 10. Energy calculated using hybrid Heitler - London - Bohr model. Solid line is based on Slater orbitals, and dashed line is based on Gaussian orbitals. Dotted line is exact energy.

energy is higher than −1 because the gaussian variational energy is higher then −1/2 for a hydrogen atom.