Alternative constraint for H_2 molecule

I. VARIATIONAL METHOD FOR H_2^+

We consider a variational wave function in the form of a superposition of hydrogenic functions centered at points A and B,

$$\psi(\boldsymbol{r}) = \phi_a(\boldsymbol{r}) + \phi_b(\boldsymbol{r}), \quad \phi_a(\boldsymbol{r}) = \exp(-r_a), \quad \phi_b(\boldsymbol{r}) = \exp(-r_b). \tag{1}$$

Then,

$$N = \int d\boldsymbol{r} \psi^2(\boldsymbol{r}) = 2\pi \left[1 + \exp(-R)\left(1 + R + R^2/3\right)\right]. \tag{2}$$

Kinetic energy equals to

$$T = -\frac{1}{2N} \int d\boldsymbol{r} \psi(\boldsymbol{r}) \boldsymbol{\nabla}^2 \psi(\boldsymbol{r}) = \frac{1}{2} - \frac{R^2 \exp(-R)}{3\sigma(R)}, \tag{3}$$

where a function σ is defined as

$$\sigma(R) = 1 + \exp(-R)\left(1 + R + R^2/3\right). \tag{4}$$

Potential energy equals to

$$V = \frac{1}{N} \int d\boldsymbol{r} \psi^2(\boldsymbol{r}) \left(-\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right) = \frac{1}{R} - \frac{2\exp(-R)(1+R)(R+\sinh R)}{R\,\sigma(R)}. \tag{5}$$

II. BOHR-LIKE METHOD FOR H_2^+

Using an empirical effective potential

$$W_{\text{eff}}(\boldsymbol{r}) = \frac{1}{2r_a^2} - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}, \tag{6}$$

the energy could be approximated as a minimum of $W_{\text{eff}}(\boldsymbol{r})$. There is no global minimum, but a local minimum exists for sufficiently large R.

III. BOHR-LIKE METHOD WITH CONSTRAINTS

We impose two constraints

$$\frac{1}{2r_a^2} = T, \quad -\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} = V. \tag{7}$$

Under the constraints (7),

$$r_a = (2T)^{-1/2}, \quad r_b = \left[\frac{1}{R} - V - (2T)^{1/2}\right]^{-1}. \tag{8}$$

It gives an approximate energy

$$W_0 = W(r_a, r_b) = T + V \tag{9}$$

which is obviously coincide with a variational energy.

IV. BOHR-LIKE METHOD FOR H_2 WITH H_2^+-INSPIRED CONSTRAINTS

We use an empirical effective potential

$$W_{\text{eff}}^{(\text{H}_2)}(\boldsymbol{r}) = \frac{1}{2r_{a1}^2} + \frac{1}{2r_{b2}^2} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} + \frac{1}{R}. \tag{10}$$

Here, we impose the constraints

$$\frac{1}{2r_{a1}^2} = T, \quad -\frac{1}{r_{a1}} - \frac{1}{r_{b1}} + \frac{1}{R} = V, \tag{11}$$

$$\frac{1}{2r_{b2}^2} = T, \quad -\frac{1}{r_{b2}} - \frac{1}{r_{a2}} + \frac{1}{R} = V, \tag{12}$$

$$\tag{13}$$

which gives a following value of $W_{\text{eff}}^{(\text{H}_2)}(\boldsymbol{r})$,

$$W_0 = 2T + 2V - 1/R + \left(2r_a^2 + 2r_b^2 - R^2\right)^{-1/2}. \tag{14}$$

In equation (14), r_a and r_b are expressed through T and V according to equation (8), and T and V are calculated using a variational expressions, equations (3) and (5). Results are shown in Figure 1.

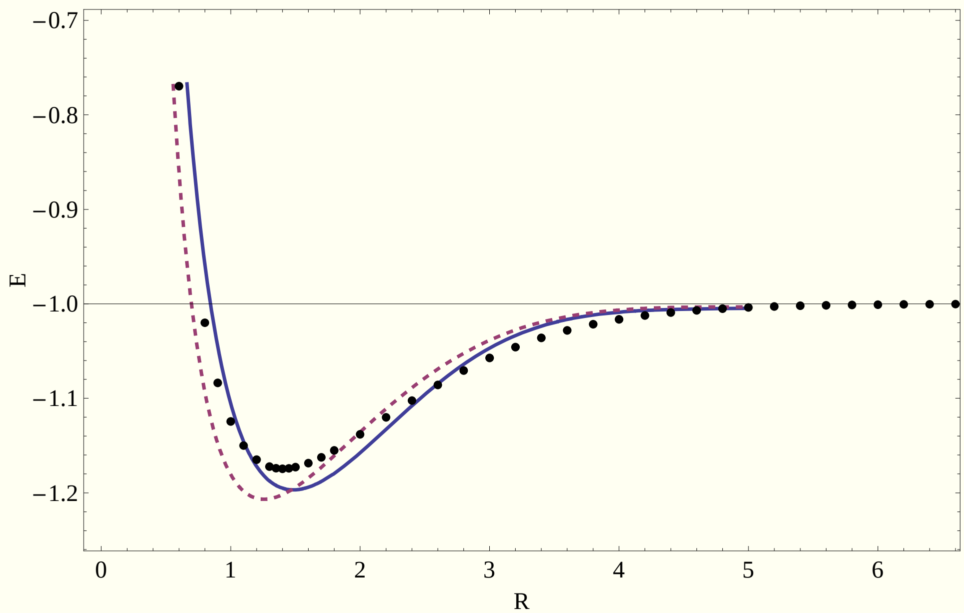

FIG. 1. Calculation of energy of H_2 molecule using constraints from H_2^+ molecule. Dots are exact energy, solid line - equation (14) using the energies T and V from a variational formulas, equations (3) and (5), and dashed line - equation (14) using exact energies T and V.