

Heitler - London model with fixed exponent orbitals and two-electron interaction from Bohr model

I. MOTIVATION

The method is designed primarily for diatomic molecules with two or three valence electrons like LiH, Li₂, H₂. It is known that Bohr model considerably over-estimates radius of alkali elements. For Li, Na and K elements Bohr model gives radius of outer electron 3.85, 8.93 and 14.61, while quantum mechanically according to a book of Slater the outer radius is 2.83, 2.93 and 4.16 respectively, in atomic units. In the current approach, we use the radius independent of nuclear separation and equal to its atomic value given by Slater. We always consider Bohr configuration of electrons where vectors \mathbf{r}_a , \mathbf{r}_b and \mathbf{R}_{AB} are orthogonal, that corresponds to Bohr approach within Hartree-Fock approximation. Since configuration is given, no minimization is performed.

II. DETAILS FOR TWO-ELECTRON DIATOMIC MOLECULE

We use Heitler - London analogue of the wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(r_{a1})\phi_b(r_{b2}) + \phi_b(r_{a1})\phi_a(r_{b2}), \quad (1)$$

In equation (1), ϕ_a and ϕ_b are Slater orbitals of radii r_a and r_b ,

$$\phi_a(r) = \exp\left(-\frac{r}{r_a}\right), \quad \phi_b(r) = \exp\left(-\frac{r}{r_b}\right). \quad (2)$$

The variational energy is constructed as an expectation value of the Hamil-

tonian over the trial wave function,

$$E = \langle \Psi | \mathbf{H} | \Psi \rangle. \quad (3)$$

The Hamiltonian is partitioned as

$$\mathbf{H} = \frac{1}{R} + \mathbf{T} + \mathbf{V}^{(1)} + \mathbf{V}^{(2)}, \quad (4)$$

where $\mathbf{T} = -\nabla_1^2/2 - \nabla_2^2/2$ is the operator of kinetic energy, $\mathbf{V}^{(1)} = -1/|\mathbf{r}_{a1}| - 1/|\mathbf{r}_{b1}| - 1/|\mathbf{r}_{a2}| - 1/|\mathbf{r}_{b2}|$ is interaction between electrons and nuclei, and $\mathbf{V}^{(2)} = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ is interaction between electrons. Respectively, the energy is partitioned as

$$E = \frac{1}{R} + \langle \mathbf{T} \rangle + \langle \mathbf{V}^{(1)} \rangle + \langle \mathbf{V}^{(2)} \rangle. \quad (5)$$

Formulas for expectation values $\langle \mathbf{T} \rangle$ and $\langle \mathbf{V}^{(1)} \rangle$ are relatively simple, they could be expressed through rational functions containing exponents, while the two-electron part $\langle \mathbf{V}^{(2)} \rangle$ is a more complicated two-electron integral that cannot be expressed through elementary functions. In the present approach, we approximate it by Bohr equivalent, $1/r_{12}$. Since we assume that $\mathbf{r}_a \perp \mathbf{r}_b, \mathbf{r}_a \perp \mathbf{R}_{AB}, \mathbf{r}_b \perp \mathbf{R}_{AB}$,

$$r_{12} = \sqrt{R^2 + r_a^2 + r_b^2}. \quad (6)$$

Our expression for energy now takes the form

$$E_{\text{Bohr}} = \frac{1}{R} + \langle \mathbf{T} \rangle + \langle \mathbf{V}^{(1)} \rangle + (R^2 + r_a^2 + r_b^2)^{-1/2}. \quad (7)$$

A. Simplest example of hydrogen molecule

Here, we take $r_a = r_b = 1$, and expression for the energy explicitly is

$$E_{\text{Bohr}} = \frac{36 - 2R(R(2R(R+3) + 3) - 18)}{R((R(R+3) + 3)^2 + 9e^{2R})} + \frac{1}{\sqrt{R^2 + 2}} - \frac{1}{R}. \quad (8)$$

The energy is plotted on Fig. 1.

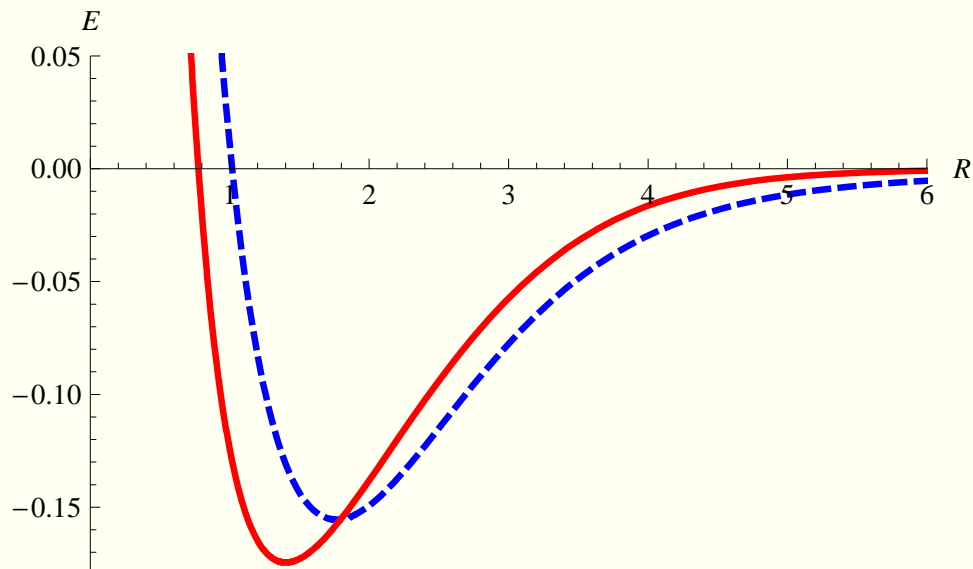


FIG. 1. Calculation of energy of H_2 molecule using approximate formula (8), dashed line. Solid line is exact energy.

B. Lithium hydride molecule

For Li H molecule, we take $r_a = 2.83$ and $r_b = 1$. The energy is plotted on Fig. 2.

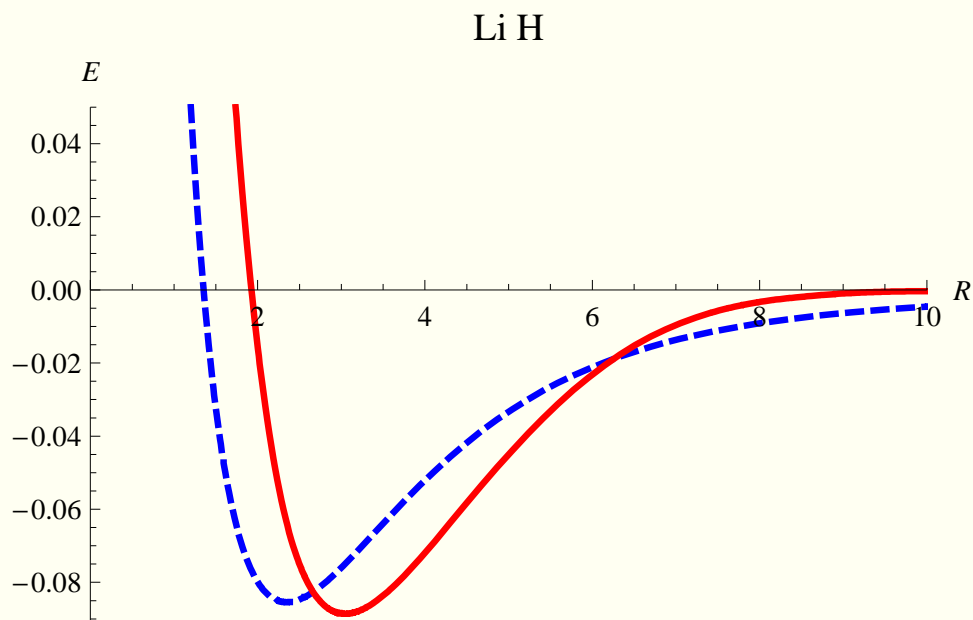
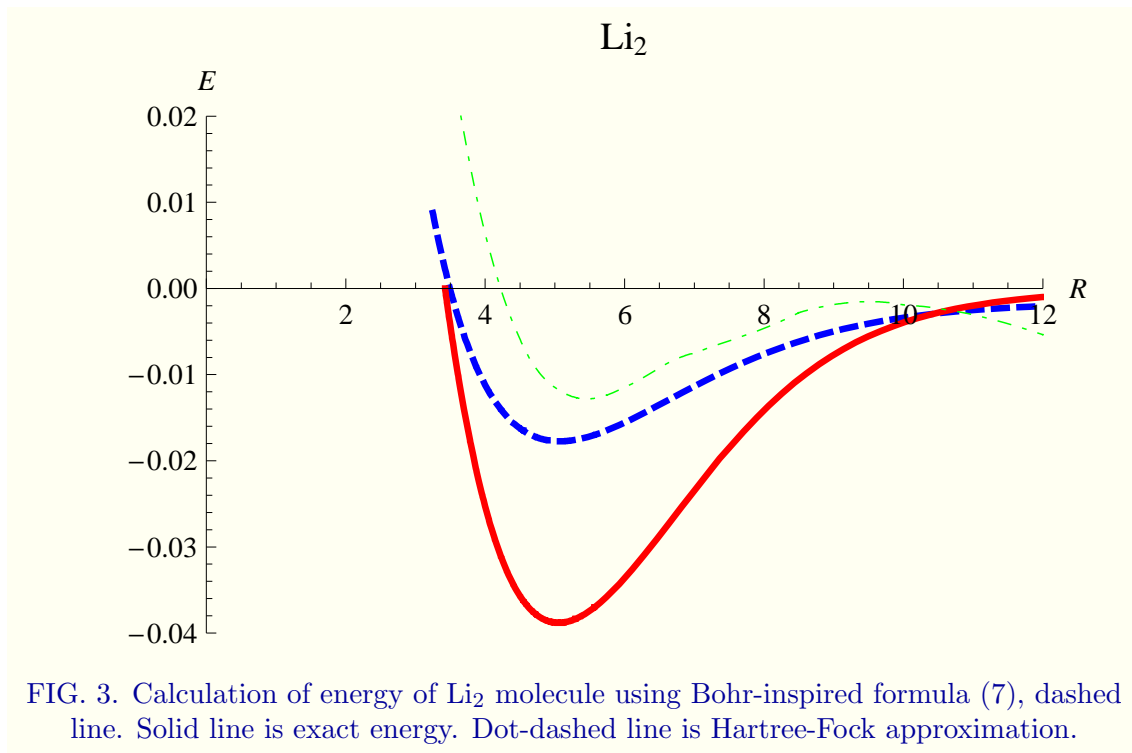


FIG. 2. Calculation of energy of Li H molecule using Bohr-inspired formula (7), dashed line. Solid line is exact energy.

C. Lithium dimer molecule

For Li_2 molecule, we take $r_a = r_b = 2.83$. The energy is plotted on Fig. 3.



III. THREE-ELECTRON DIATOMIC MOLECULES

As it was shown in [1], taking into account spins is equivalent to choosing a spinless trial wave function (should be checked)

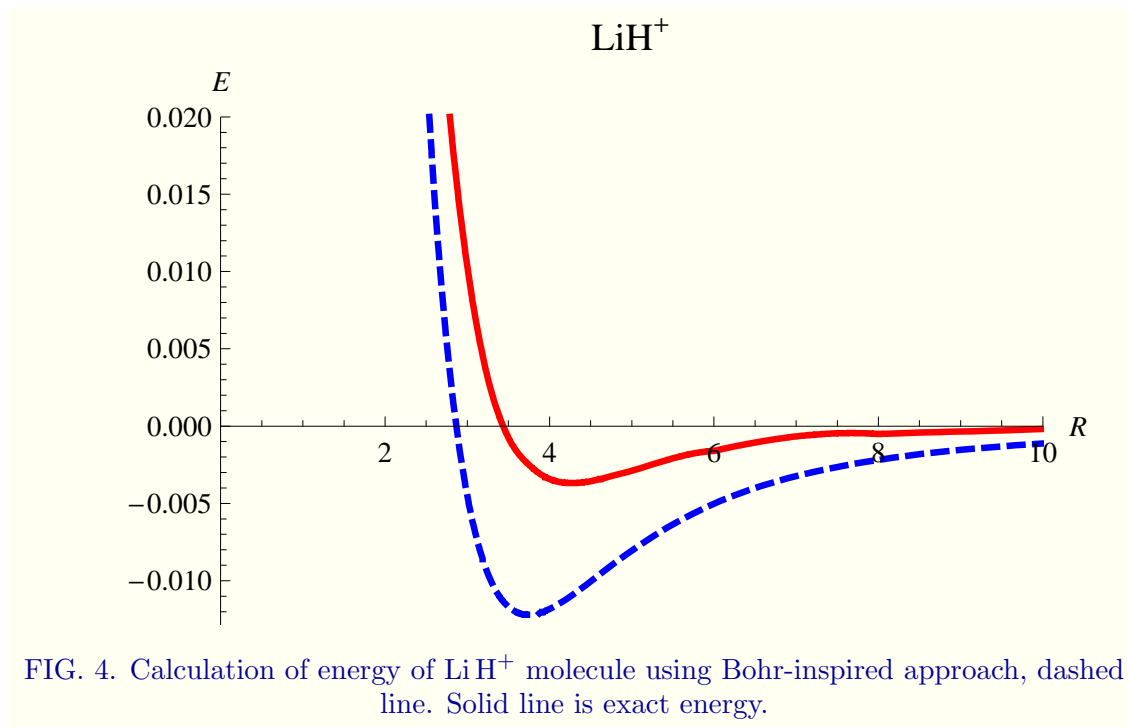
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \phi_a(r_{a1})\phi_a(r_{a2})\phi_b(r_{b3}) - \phi_a(r_{a1})\phi_a(r_{a3})\phi_b(r_{b2}). \quad (9)$$

The energy is calculated by equation (5), with $\langle V^{(2)} \rangle$ replaced by its Bohr equivalent $1/r_{12} + 1/r_{13} + 1/r_{23}$, and

$$r_{12} = \sqrt{2}r_a, \quad r_{13} = r_{23} = \sqrt{R^2 + r_a^2 + r_b^2}. \quad (10)$$

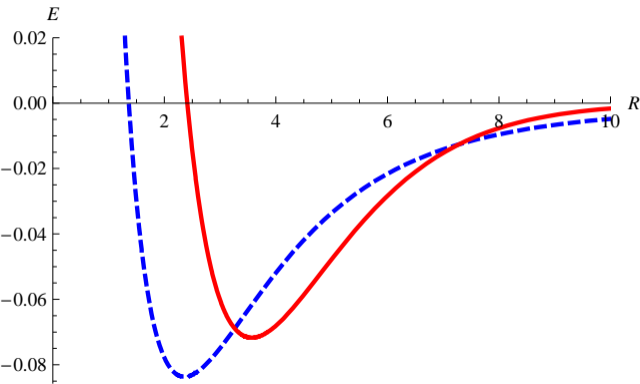
A. LiH^+ molecule

Here, we take $r_a = 0.364$ and $r_b = 1$. The energy is plotted on Fig. 4.

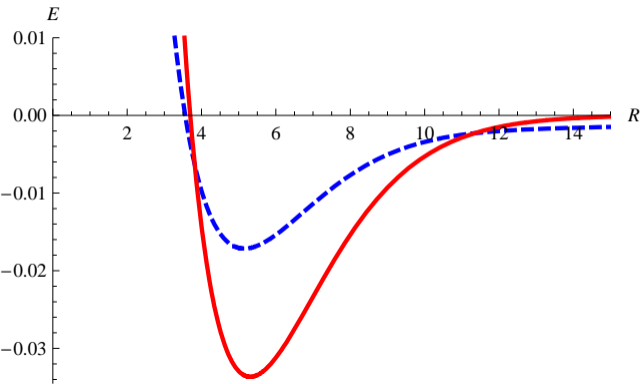


[1] E. B. Wilson, Jr., J. Chem. Phys, **1**, 210 (1933).

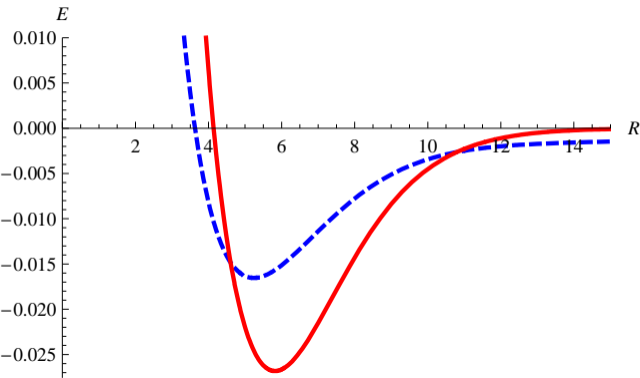
NaH



NaLi



NaNa



Li H

