

**Re-examining the paper "Model of molecular bonding based on
the Bohr - Sommerfeld picture of atoms", Phys. Lett. A 355, 373
(2006)**

I. DERIVATION OF THE CONSTRAINT

A "constraint model" was introduced in an attempt to make a previously formulated "nearest nucleus quantization model" working at small separation distances R . The latter model (quantization relative to the nearest nucleus) is derived by itself from the original Bohr model at *large* separation distances R (two weakly interacting H atoms). It seems that there is some inconsistency in an attempt to use a large- R model for small R . It is not quite clear how the additional large- R approximation could make the original Bohr model work better for small R . What happens if we apply the constraint directly to the original Bohr model (without introducing any additional approximations)?

A constraint is introduced in the paper as

$$-\frac{1}{r_{b1}} = \Phi(r, R), \quad (1)$$

see Equation (5) of the paper.

The function $\Phi(r, R)$ is defined in the paper originally as

$$\Phi(r, R) = \left\langle \Psi \left| -\frac{1}{r_{b1}} \right| \Psi \right\rangle, \quad (2)$$

see Equation (4) of the paper.

Below, we give formulas necessary to derive this expectation value. Slater orbital of radius \bar{r} is defined as

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{\pi\bar{r}^3}} \exp\left(-\frac{r}{\bar{r}}\right). \quad (3)$$

In Heitler - London model, a variational trial function is defined as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2(1+S^2)}} [\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)], \quad (4)$$

where

$$\phi_a(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{R}_a), \quad \phi_b(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{R}_b), \quad |\mathbf{R}_a - \mathbf{R}_b| = R, \quad (5)$$

and the overlap integral is

$$S = \int d\mathbf{r} \phi_a(\mathbf{r})\phi_b(\mathbf{r}) = \exp\left(-\frac{R}{r}\right) \left(1 + \frac{R}{r} + \frac{1}{3} \frac{R^2}{r^2}\right). \quad (6)$$

A bar over r is omitted henceforward.

The function $\Phi(r, R)$ as defined by equation (2) is expressed through one-electron Coulomb integrals as

$$\Phi = -\frac{f + 2Sg + 1/r}{2(1 + S^2)}, \quad (7)$$

where Coulomb integrals are

$$f = \left\langle \phi_a \left| \frac{1}{r_b} \right| \phi_a \right\rangle = \frac{1}{R} - \exp\left(-\frac{2R}{r}\right) \left(\frac{1}{R} + \frac{1}{r}\right), \quad (8)$$

$$g = \left\langle \phi_a \left| \frac{1}{r_b} \right| \phi_b \right\rangle = \frac{1}{r} \exp\left(-\frac{R}{r}\right) \left(1 + \frac{R}{r}\right). \quad (9)$$

In the numerator in the right hand side of equation (11), there are four terms in total, f , $2 \times Sg$, and $-1/r$, originating from integrating of four terms of Ψ^2 in equation (2).

In contrast, a function $\Phi(r, R)$ that is used in subsequent calculations of the "constraint Bohr model" has only two terms. It is given by Equation (8) from the paper,

$$\Phi = -\frac{f + Sg}{1 + S^2}. \quad (10)$$

It would be desirable for further applications to understand the way how the final formula (17) was derived. It is interesting to note that keeping all four terms in equation (2) or just discarding only one "nearest atom interaction term" $1/r$ does not give meaningful results for the energy.

Similarly, for Hund - Mulliken model, the function $\Phi(r, R)$ as defined by equation (2) is expressed through one-electron Coulomb integrals as

$$\Phi = -\frac{f + 2g + 1/r}{2(1 + S)}, \quad (11)$$

but for some unexplained reason, only two terms $f + g$ are left in the final formula (11) from the paper,

$$\Phi = -\frac{f + g}{1 + S}. \quad (12)$$

II. APPLICATION OF "CONSTRAINT BOHR MODEL" FOR A HYDROGEN MOLECULE

The method reduces to finding of a minimum of the function

$$W(\rho, x) = \frac{1}{\rho^2 + x^2} - \frac{2}{\sqrt{\rho^2 + x^2}} - \frac{2}{\sqrt{\rho^2 + (R - x)^2}} + \frac{1}{\sqrt{4\rho^2 + (R - 2x)^2}} + \frac{1}{R} \quad (13)$$

under the constraint

$$-\frac{2}{\sqrt{\rho^2 + (R - x)^2}} = \Phi(\sqrt{\rho^2 + x^2}, R). \quad (14)$$

It seems that the constraint Bohr model offers an accurate method for the ground state energy of a hydrogen molecule, see Figure 1. It is more accurate than the original Bohr model for $R > 1$. Unlike "nearest nucleus quantization", it works for small $R < 2.7$. Notice that both HL-based formula for the constraint potential Φ , equation (17), and HM formula, equation (12), produce comparable accuracy ~ 0.01 Hartree.

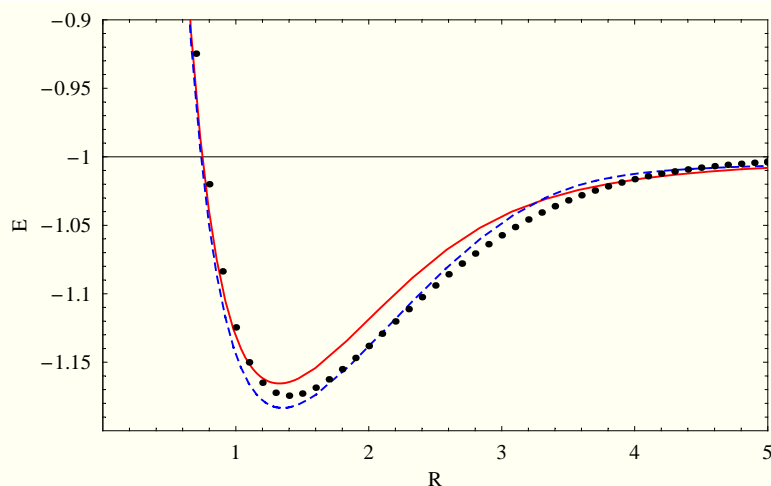


FIG. 1. Constraint Bohr model for a hydrogen molecule. Solid line is based on Heitler - London model, and dashed line is based on Hund - Mulliken model, equations (17) and (12) respectively. Dotted line is exact energy.

III. THREE HYDROGEN ATOMS

A. Linear configuration

The way of applying constraints based on two-atom variational model for the case of three and more atoms is not quite clear.

The method reduces to finding of a minimum of the function

$$W(\rho, \rho_1, x) = \frac{1}{\rho^2 + x^2} + \frac{1}{2\rho_1^2} - \frac{1}{|\rho_1|} - \frac{2}{\sqrt{R^2 + \rho_1^2}} - \frac{2}{\sqrt{\rho_1^2 + (R-x)^2}} + \frac{1}{2|R-x|} - \frac{2}{\sqrt{\rho^2 + x^2}} - \frac{2}{\sqrt{\rho^2 + (2R-x)^2}} + \frac{2}{\sqrt{(\rho + \rho_1)^2 + (R-x)^2}} + \frac{5}{2R} \quad (15)$$

under the constraint

$$-\frac{2}{\sqrt{\rho^2 + (R-x)^2}} - \frac{2}{\sqrt{\rho^2 + (2R-x)^2}} = \Phi(\sqrt{\rho^2 + x^2}, R) + \Phi_t(\sqrt{\rho^2 + x^2}, 2R), \quad (16)$$

where

$$\Phi_t = -\frac{f - Sg}{1 - S^2}. \quad (17)$$

Results obtained in the paper are shown by a dashed line in Figure 2. Results obtained with Heitler - London constraint are not given in the paper. It appears ten times less accurate than the result with Hund - Mulliken constraint. It would be desirable to give

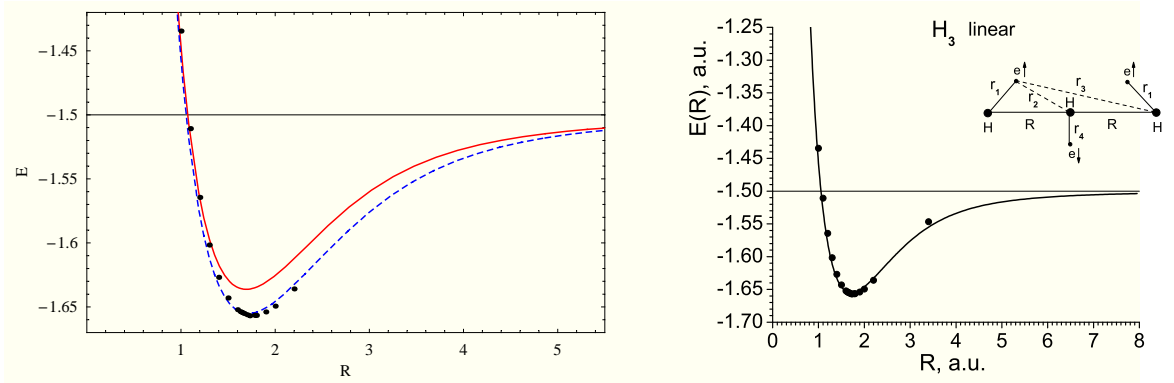


FIG. 2. Constraint Bohr model for three hydrogen atoms in linear configuration. Left panel shows both Heitler - London model and Hund - Mulliken model, solid and dashed lines respectively. Dots are exact energy. Right panel is a reproduction of Fig. 5 from the paper, with only one HM curve shown.

some recipe how to choose an appropriate model from two available models (HL and HM) that are otherwise considered on equal footing.

For the second electron, since its x -coordinate is fixed, "there is no collapse and therefore no need for any constraint". This phrase implies that even if the second constraint is imposed, results will not be worse, just calculations will be excessive. In fact, imposing the second constraint gives completely meaningless results, $E > -1.5$.

B. Triangular configuration

Results obtained in the paper are shown by a dashed line in Figure 3 (Hund - Mulliken constraint). Results obtained with Heitler - London constraint (not given in the paper) appear to give around the same accuracy in this case.

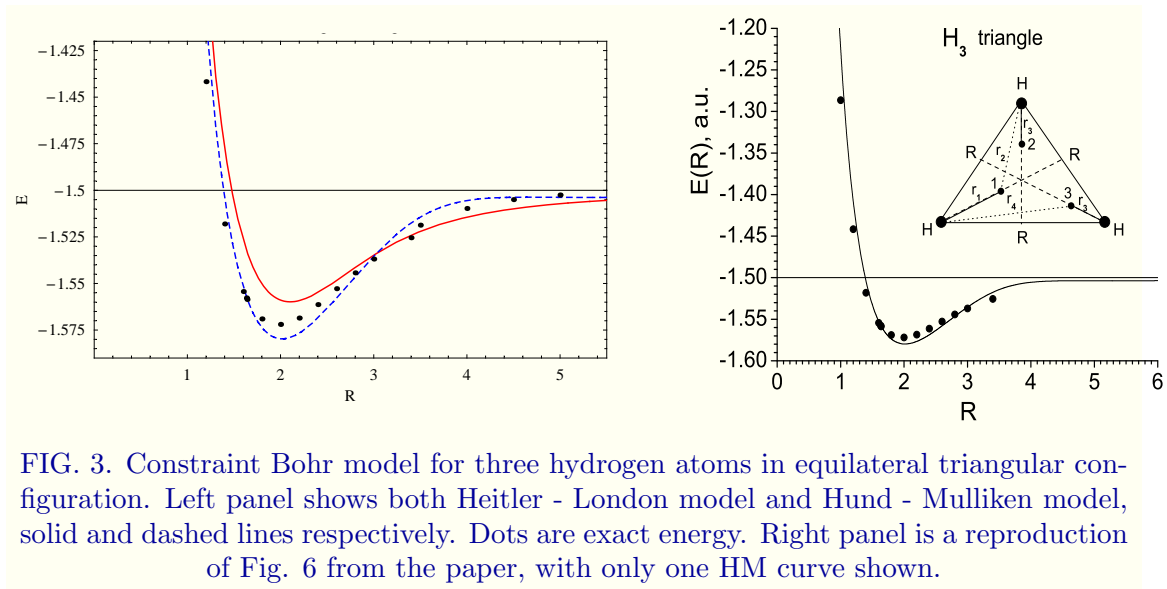


FIG. 3. Constraint Bohr model for three hydrogen atoms in equilateral triangular configuration. Left panel shows both Heitler - London model and Hund - Mulliken model, solid and dashed lines respectively. Dots are exact energy. Right panel is a reproduction of Fig. 6 from the paper, with only one HM curve shown.

C. Molecule Be_2

”The beryllium dimer is a notoriously difficult molecule which attracted the attention of many theoreticians... Even sophisticated ab initio methods failed for a long time to correctly describe the bond in Be_2 .”, according to a paper in Chem. Phys. 185, 47 (1994). ”Limited configuration interaction (CI) calculations including only single and double excitations give a shallow minimum ($0.2 mE_h$) around 8.5 bohr”, from Chem. Phys. Lett. 160, 494 (1989). It seems from this point of view, that even limited accuracy achieved by a simple Bohr model combined with a primitive variational model for hydrogen represents an impressive fact.

Here, the constraint derived originally for 1s orbital is applied for a combination of 1s, 2s, and 2p orbitals.

Unpublished notes of A.S. et al. (2005) give details of calculations that are not mentioned in the paper. A sophisticated constraint is based on a controversial assumption that ”the two outer Be electrons are in 2s2p state and have parallel spins”.

Results obtained with HL and HM constraints are shown in Figure 4, together with the result shown in the paper. Both HL and HM constraints don't in fact give binding energy,

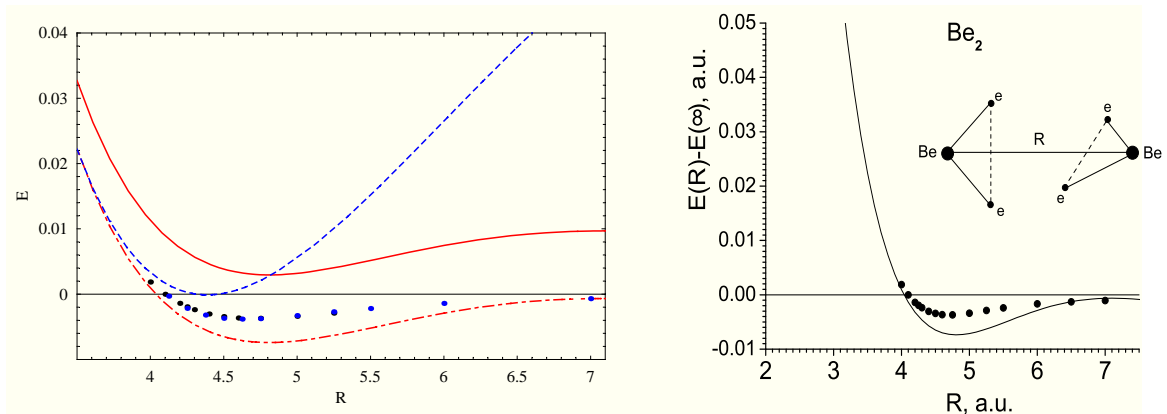


FIG. 4. Dissociation energy $E(R) - E(\infty)$ for the constraint Bohr model for Be_2 molecule. Left panel shows both Heitler - London model and Hund - Mulliken model, solid and dashed lines respectively. Dots are exact and experimental energy. Dot-dashed line is HL model curve shifted along the vertical axis. Right panel is a reproduction of Fig. 7 from the paper, with only the vertically shifted HL curve shown.

since both curves lie above $E = 0$ line. As it is indicated in the unpublished notes, the curve shown on Fig. 7 from the paper is in fact HL curve with some vertical negative offset, since "we also have shifted the Bohr model curve vertically to match it with "exact" dot at $R = 7$ ". It seems that in fact both HL curve (without a premediated offset) and HM curve (even with any offset) fail in the case of Be_2 molecule. It should be noted however, that both curves predict location of the minimum with accuracy of 10 - 20%.