

Hybrids of Heitler - London model with Bohr model for three-electron molecules

I. VARIATIONAL WAVE FUNCTION

We construct the Slater determinant from one-electron hydrogenic wave functions (Slater orbitals) as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \begin{vmatrix} \alpha(1)\psi_a(\mathbf{r}_1) & \alpha(2)\psi_a(\mathbf{r}_2) & \alpha(3)\psi_a(\mathbf{r}_3) \\ \alpha(1)\psi_b(\mathbf{r}_1) & \alpha(2)\psi_b(\mathbf{r}_2) & \alpha(3)\psi_b(\mathbf{r}_3) \\ \beta(1)\psi_c(\mathbf{r}_1) & \beta(2)\psi_c(\mathbf{r}_2) & \beta(3)\psi_c(\mathbf{r}_3) \end{vmatrix}. \quad (1)$$

Coordinate components of one-electron wave functions are

$$\psi_a(\mathbf{r}) = \frac{1}{\sqrt{\pi r_1^3}} \exp(-|\mathbf{r} - \mathbf{R}_a|/r_1), \quad (2)$$

$$\psi_b(\mathbf{r}) = \frac{1}{\sqrt{\pi r_2^3}} \exp(-|\mathbf{r} - \mathbf{R}_b|/r_2), \quad (3)$$

$$\psi_c(\mathbf{r}) = \frac{1}{\sqrt{\pi r_3^3}} \exp(-|\mathbf{r} - \mathbf{R}_c|/r_3). \quad (4)$$

There are three variational parameters, r_1 , r_2 , and r_3 , that correspond to the nearest-atom distances in the associated Bohr model. Two-component vectors $\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ correspond to spin-up and spin-down states.

Expanding the determinant (1) and collecting spin functions, we obtain

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \beta(1)\alpha(2)\alpha(3)\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \alpha(1)\beta(2)\alpha(3)\Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \alpha(1)\alpha(2)\beta(3)\Psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (5)$$

where the spinless function entering equation (5) are

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi_c(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_3) - \psi_c(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\psi_a(\mathbf{r}_3), \quad (6)$$

$$\Psi_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi_b(\mathbf{r}_1)\psi_c(\mathbf{r}_2)\psi_a(\mathbf{r}_3) - \psi_a(\mathbf{r}_1)\psi_c(\mathbf{r}_2)\psi_b(\mathbf{r}_3), \quad (7)$$

$$\Psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\psi_c(\mathbf{r}_3) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\psi_c(\mathbf{r}_3). \quad (8)$$

An expectation value of any spinless operator \hat{A} could be calculated as

$$\langle \hat{A} \rangle = \frac{\langle \Psi_1 | \hat{A} | \Psi_1 \rangle + \langle \Psi_2 | \hat{A} | \Psi_2 \rangle + \langle \Psi_3 | \hat{A} | \Psi_3 \rangle}{\langle \Psi_1 | \Psi_1 \rangle + \langle \Psi_2 | \Psi_2 \rangle + \langle \Psi_3 | \Psi_3 \rangle}. \quad (9)$$

Particularly, the expectation value of the kinetic energy is

$$\begin{aligned} T_{\text{var}}(r_1, r_2, r_3) &= \langle \frac{1}{2} \nabla_1^2 + \frac{1}{2} \nabla_2^2 + \frac{1}{2} \nabla_3^2 \rangle \\ &= \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} + \frac{1}{r_3^2} + \frac{64r_1r_2}{r_1^4 + 8r_2r_1^3 + 30r_2^2r_1^2 + 8r_2^3r_1 + r_2^4} \right). \end{aligned} \quad (10)$$

This expression was written for the case when $\mathbf{R}_1 = \mathbf{R}_2 = \mathbf{R}_3$. It is more lengthy for a general case. Notice the last term in the r.h.s. of equation (10) is the correction to the nearest-atom quantization Bohr kinetic energy, which is $\frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} + \frac{1}{r_3^2} \right)$. Consider for a moment that we take a spinless Hartree wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\psi_c(\mathbf{r}_3)$ instead of (1). Then the kinetic energy is just $\frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} + \frac{1}{r_3^2} \right)$. It means that the correction $\frac{64r_1r_2}{r_1^4 + 8r_2r_1^3 + 30r_2^2r_1^2 + 8r_2^3r_1 + r_2^4}$ includes exchange integrals, and it appears as a result of choice of spins.

II. HYBRID MODEL

The energy is defined as

$$E_{\text{var-B}}(R) = \min_{r_1, r_2, r_3} [T_{\text{var}}(r_1, r_2, r_3) + V_{\text{B}}(r_1, r_2, r_3)], \quad (11)$$

where $T_{\text{var}}(r_1, r_2, r_3)$ is given by equation (10), and $V_{\text{B}}(r_1, r_2, r_3)$ is taken from the Bohr model.

III. RESULTS FOR LITHIUM

Here, I consider the united-atom limit when $\mathbf{R}_1 = \mathbf{R}_2 = \mathbf{R}_3$. Then, the kinetic energy is given by equation (10). For the potential energy, I choose the expression that is derived in case of an orthogonal configuration corresponding to weakly interacting electrons ($\mathbf{r}_1 \perp \mathbf{r}_2$, $\mathbf{r}_2 \perp \mathbf{r}_3$, and $\mathbf{r}_3 \perp \mathbf{r}_1$),

$$V_{\text{B}}(r_1, r_2, r_3) = -\frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{\sqrt{r_1^2 + r_2^2}} + \frac{1}{\sqrt{r_2^2 + r_3^2}} + \frac{1}{\sqrt{r_3^2 + r_1^2}}. \quad (12)$$

The minimum of the energy functional (11) gives $E = -7.133$ at $r_1 = r_3 = 0.38$ and $r_2 = 4.36$. The accuracy is poor. The exact energy for lithium is -7.438 . Similar poor results (without even a minimum on the energy surface) are obtained for the system H_3 , both in the linear and in the triangle configurations. Currently, I am checking derivations for possible errors.