Using orthogonality to take into account Pauli exclusion principle

I. LOWEST STATES WITH $n = 1, 2$

Ground state orbital is modeled by a function

$$\phi_1(r) = e^{-r/r_1}. \tag{1}$$

Excited state orbital is modeled by a function

$$\phi_2(r) = e^{-r/r_2} - \left(\frac{2r_2}{r_1 + r_2}\right)^3 e^{-r/r_1}. \tag{2}$$

II. ORTHOGONALITY PROPERTY

Functions $\phi_1(r)$ and $\phi_2(r)$ are orthogonal,

$$\int_0^\infty r^2\, \phi_1(r)\phi_2(r)\, dr = 0. \tag{3}$$

III. EXPECTATION VALUES OF $1/r$

Expectation values of $1/r$ equal to $1/r_1$ and $1/r_2$, for the functions $\phi_1(r)$ and $\phi_2(r)$ respectively,

$$\left\langle \phi_1 \left| \frac{1}{r} \right| \phi_1 \right\rangle = \frac{1}{r_1}, \quad \left\langle \phi_2 \left| \frac{1}{r} \right| \phi_2 \right\rangle = \frac{1}{r_2}. \tag{4}$$

Note that that expectation value of $\phi_2(r)$ is the same as if the second term in equation (2) is absent.

IV. KINETIC ENERGY

Kinetic energy operator is

$$T = -\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr}. \tag{5}$$

Expectation values of kinetic energy are

$$T_1 \equiv \langle \phi_1 | T | \phi_1 \rangle = \frac{1}{2r_1^2}, \tag{6}$$

$$T_2 \equiv \langle \phi_2 | T | \phi_2 \rangle = \frac{1}{2r_2^2} + \frac{32 r_1 r_2}{r_1^4 + 8r_1^3 r_2 + 30 r_1^2 r_2^2 + 8 r_1 r_2^3 + r_2^4}. \tag{7}$$

Note that $T_1 + T_2$ is a symmetric function of its arguments, r_1 and r_2.

V. 1s 2s STATE OF HELIUM ATOM

In 1s 2s state of helium, the second orbital corresponds to the first excited state, which should be orthogonal to the orbital, corresponding to the ground state. Accordingly, we use orbitals ϕ_1 and ϕ_2, equations (1) and (2), to describe electrons in 1s s state of helium. The functional of energy is

$$W(r_1, r_2) = T(r_1, r_2) + V(r_1, r_2), \tag{8}$$

where

$$T = T_1 + T_2, \tag{9}$$

$$V = -2/r_1 - 2/r_2 + 1/(r_1 + r_2), \tag{10}$$

T_1 and T_2 are given by equations (6) and (7), and we consider $\theta = 180°$ electronic configuration, e.g. when electrons are located from opposite sides of the nucleus.

Minimization of the function $W(r_1, r_2)$ gives $E = W_{\text{min}} = -2.14669$ at $r_1 = 0.501$ and $r_2 = 3.686$. The energy is only 0.03% lower than the energy -2.145974 of $2\,^1$S state and 1.3% higher than the energy -2.175229 of $2\,^3$S state.

For comparison, in "Bohr-model" approach, we minimize a function

$$W^{(\text{Bohr})}(r_1, r_2) = T^{(\text{Bohr})}(r_1, r_2) + V(r_1, r_2), \tag{11}$$

$$T^{(\text{Bohr})}(r_1, r_2) = T_1^{(\text{Bohr})} + T_2^{(\text{Bohr})}, \quad T_1^{(\text{Bohr})} = \frac{1}{2r_1^2}, \quad T_2^{(\text{Bohr})} = \frac{2}{r_2^2}. \tag{12}$$

Minimization of Bohr function gives $E = W_{\text{min}}^{(\text{Bohr})} = -2.1596$ at $r_1 = 0.505$ and $r_2 = 3.188$. The energy is 0.6% lower than the energy -2.145974 of $2\,^1$S state and 0.7% higher than the energy -2.175229 of $2\,^3$S state.

For reference, we give results of minimization of the function W for different angles θ (which affects only the formula for the inter-electron potential).

VI. Li H MOLECULE

Let us consider four orbitals,

$$\phi_1(\boldsymbol{r}) = \phi_2(\boldsymbol{r}) = e^{-r_a/r_1}, \tag{13}$$

$$\phi_3(\boldsymbol{r}) = e^{-r_a/r_3}\left(1 - \lambda_3 r_a\right), \tag{14}$$

$$\phi_4(\boldsymbol{r}) = e^{-r_b/r_4}\left(1 - \lambda_4 r_b\right), \tag{15}$$

TABLE I. Minimization of the function $W(r_1, r_2)$ for different angles θ

θ	V_{12}	$r_1^{(0)}$	$r_2^{(0)}$	E	$\% E(2\,^1\mathrm{S})$	$\% E(2\,^3\mathrm{S})$
180°	$\frac{1}{r_1+r_2}$	0.501	3.686	-2.1467	100.03%	98.7%
90°	$\frac{1}{\sqrt{r_1^2+r_2^2}}$	0.498	4.469	-2.1216	98.9%	97.5%
0°	$\frac{1}{\lvert r_1-r_2\rvert}$	0.495	5.608	-2.0988	97.8%	96.5%

TABLE II. Minimization of the function $W^{(\mathrm{Bohr})}(r_1, r_2)$ for different angles θ

θ	V_{12}	$r_1^{(0)}$	$r_2^{(0)}$	E	$\% E(2\,^1\mathrm{S})$	$\% E(2\,^3\mathrm{S})$
180°	$\frac{1}{r_1+r_2}$	0.505	3.188	-2.1596	100.6%	99.3%
90°	$\frac{1}{\sqrt{r_1^2+r_2^2}}$	0.501	3.906	-2.1270	99.1%	97.8%
0°	$\frac{1}{\lvert r_1-r_2\rvert}$	0.497	5.159	-2.0980	97.8%	96.4%

where r_1, r_3, and r_4 are free minimization parameters. Parameters λ_3 and λ_4 are chosen in order to make ϕ_3 and ϕ_4 orthogonal to ϕ_1 and ϕ_2,

$$\lambda_3 = \frac{1}{3}\left(\frac{1}{r_1} + \frac{1}{r_3}\right),$$

$$\lambda_4 = \frac{(r_1^2 - r_4^2)\left(e^{\frac{R}{r_4}} r_1 \left(R r_1^2 - (R + 4r_1)\, r_4^2\right) + e^{\frac{R}{r_1}} r_4 \left(4 r_4 r_1^2 + R\left(r_1^2 - r_4^2\right)\right)\right)}{r_4 \left(e^{\frac{R}{r_1}} \left(8 R r_4 \left(r_1^2 - r_4^2\right) r_1^2 + 4 r_4^2 \left(5 r_1^2 + r_4^2\right) r_1^2 + R^2 \left(r_1^2 - r_4^2\right)^2\right) - e^{\frac{R}{r_4}} r_1 \left(-3 R r_1^4 + 2\left(R + 10 r_1\right) r_4^2 r_1^2 + (\right.\right.}$$

For each orbital ϕ_i, we consider a point on a circle at distance $\bar{r}_{ai}$ from a point A and at distance $\bar{r}_{bi}$ from a point B, where

$$\frac{1}{\bar{r}_{ai}} = \langle\phi_i|\, \frac{1}{r_a}\, |\phi_i\rangle\,, \tag{18}$$

$$\frac{1}{\bar{r}_{bi}} = \langle\phi_i|\, \frac{1}{r_b}\, |\phi_i\rangle\,. \tag{19}$$

Distances $\bar{r}_{ai}$ and $\bar{r}_{bi}$ are as follows

$$\bar{r}_{a1} = \bar{r}_{a2} = r_1, \tag{20}$$

$$\bar{r}_{b1} = \bar{r}_{b2} = \frac{R}{1 - \frac{e^{-\frac{2R}{r_1}}(R+r_1)}{r_1}}, \tag{21}$$

$$\bar{r}_{a3} = \frac{2r_3\left(3r_3\lambda_3\left(r_3\lambda_3-1\right)+1\right)}{r_3\lambda_3\left(3r_3\lambda_3-4\right)+2}, \tag{22}$$

$$\bar{r}_{b3} = \frac{2e^{\frac{2R}{r_3}}Rr_3\left(3r_3\lambda_3\left(r_3\lambda_3-1\right)+1\right)}{-2\lambda_3^2R^3+2\lambda_3\left(2-3r_3\lambda_3\right)R^2+\left(r_3\lambda_3\left(8-9r_3\lambda_3\right)-2\right)R+2\left(-1+e^{\frac{2R}{r_3}}\right)r_3\left(3r_3\lambda_3\left(r_3\lambda_3-1\right)+1\right)}, \tag{23}$$

$$\bar{r}_{a4} = \frac{2e^{\frac{2R}{r_4}}Rr_4\left(3r_4\lambda_4\left(r_4\lambda_4-1\right)+1\right)}{-2\lambda_4^2R^3+2\lambda_4\left(2-3r_4\lambda_4\right)R^2+\left(r_4\lambda_4\left(8-9r_4\lambda_4\right)-2\right)R+2\left(-1+e^{\frac{2R}{r_4}}\right)r_4\left(3r_4\lambda_4\left(r_4\lambda_4-1\right)+1\right)}, \tag{24}$$

$$\bar{r}_{b4} = \frac{2r_4\left(3r_4\lambda_4\left(r_4\lambda_4-1\right)+1\right)}{r_4\lambda_4\left(3r_4\lambda_4-4\right)+2}. \tag{25}$$

After substitution of λ_3 we obtain

$$\bar{r}_{a3} = 2\left(-\frac{3r_1^3}{3r_1^2-2r_3r_1+r_3^2}+r_1+r_3\right), \tag{26}$$

$$\bar{r}_{b3} = \frac{6e^{\frac{2R}{r_3}}Rr_3^3\left(r_1^2-r_3r_1+r_3^2\right)}{-2\left(r_1+r_3\right)^2R^3+6r_3\left(r_1^2-r_3^2\right)R^2-3r_3^2\left(r_1^2-2r_3r_1+3r_3^2\right)R+6\left(-1+e^{\frac{2R}{r_3}}\right)r_3^3\left(r_1^2-r_3r_1+r_3^2\right)} \tag{27}$$

Expectation values of kinetic energy for ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are

$$T_1 = T_2 = \frac{1}{2r_1^2}, \tag{28}$$

$$T_3 = \frac{7r_1^2-r_3r_1+r_3^2}{6r_3^2\left(r_1^2-r_3r_1+r_3^2\right)}, \tag{29}$$

$$T_4 = \frac{r_4\lambda_4\left(r_4\lambda_4-1\right)+1}{2r_4^2\left(3r_4\lambda_4\left(r_4\lambda_4-1\right)+1\right)}. \tag{30}$$

Total kinetic energy is

$$T = T_1 + T_2 + T_3 + T_4 \tag{31}$$

Potential energy is

$$V = V^{(0)} + V^{(1)} + V^{(2)}, \tag{32}$$

where

$$V^{(0)} = \frac{3}{R}, \tag{33}$$

$$V^{(1)} = -\frac{3}{r_{a1}}-\frac{1}{r_{b1}}-\frac{3}{r_{a2}}-\frac{1}{r_{b2}}-\frac{3}{r_{a3}}-\frac{1}{r_{b3}}-\frac{3}{r_{a4}}-\frac{1}{r_{b4}}, \tag{34}$$

$$V^{(2)} = \frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{14}}+\frac{1}{r_{23}}+\frac{1}{r_{24}}+\frac{1}{r_{34}}. \tag{35}$$

Total energy is

$$W = T + V. \tag{36}$$

It is to be minimized with eight constraints,

$$r_{a1} = \bar{r}_{a1}, \quad r_{b1} = \bar{r}_{b1}, \quad r_{a2} = \bar{r}_{a2}, \quad r_{b2} = \bar{r}_{b2}, \quad r_{a3} = \bar{r}_{a3}, \quad r_{b3} = \bar{r}_{b3}, \quad r_{a4} = \bar{r}_{a4}, \quad r_{b4} = \bar{r}_{b4}. \tag{37}$$

A. Numerical results of minimization

We express vectors $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, $\boldsymbol{r}_3$, $\boldsymbol{r}_4$ through 8 coordinates $x_1, x_2, y_2, x_3, y_3, z_3, x_4, y_4, z_4$ as

$$\boldsymbol{r}_1 = (x_1, 0, 0), \quad \boldsymbol{r}_2 = (x_2, y_2, 0), \quad \boldsymbol{r}_3 = (x_3, y_3, z_3), \quad \boldsymbol{r}_4 = (x_4, y_4, z_4). \tag{38}$$

Then, we minimize W with constraints in respect to 8 coordinates and 3 parameters r_1, r_3, r_4.