

Possible combinations of Heitler - London model with Bohr model

I. PRELIMINARY REMARKS

All models are considered for a hydrogen molecule.

II. HEITLER - LONDON MODEL

The energy is defined as

$$E_{\text{HL}}(R) = \min_r W_{\text{HL}}(r, R). \quad (1)$$

In equation (1), $W_{\text{HL}}(r, R)$ is the HL variational energy functional, R is the separation distance between two nuclei, and r is a variational parameter. It is more conventional to use a variational parameter α instead of the parameter r . In our notations, $r = 1/\alpha$. It equals to the expectation value of radius for the Slater orbital $\psi(\mathbf{r}) = \sqrt{\alpha^3/\pi} \exp(-\alpha|\mathbf{r}|)$ (in this formula, the vector \mathbf{r} should not be confused with the parameter r !). The HL variational function is chosen as a symmetrized product of two Slater orbitals centered on the first and on the second nucleus, $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ respectively:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(r, R)}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)], \quad (2)$$

where $N(r, R)$ is the normalization factor

$$N(r, R) = (1 + S^2(R/r))^{-1/2}, \quad (3)$$

and $S(R/r)$ is the overlap integral between the orbitals $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$,

$$S(w) = e^{-w} (1 + w + w^2/3). \quad (4)$$

The variational functional is constructed as an expectation value of the Hamiltonian over the trial wave function,

$$W_{\text{HL}}(r, R) = \langle \Psi | \mathbf{H} | \Psi \rangle. \quad (5)$$

The Hamiltonian is partitioned as

$$\mathbf{H} = \frac{1}{R} + \mathbf{T} + \mathbf{V}^{(1)} + \mathbf{V}^{(2)}, \quad (6)$$

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

$$W_{\text{HL}}(r, R) = \frac{1}{R} + T_{\text{HL}}(r, R) + V_{\text{HL}}^{(1)}(r, R) + V_{\text{HL}}^{(2)}(r, R). \quad (7)$$

Explicit formulas for the functions $T_{\text{HL}}(r, R)$, $V_{\text{HL}}^{(1)}(r, R)$, and $V_{\text{HL}}^{(2)}(r, R)$ are given below. While calculation of $T_{\text{HL}}(r, R)$ and $V_{\text{HL}}^{(1)}(r, R)$ reduces to a three dimensional integral over the coordinate space of one electron, the calculation of $V_{\text{HL}}^{(2)}(r, R)$ reduces to a more complex six dimensional integral over the coordinate space of two electrons.

$$T_{\text{HL}}(r, R) = \frac{9 \left(1 + e^{\frac{2R}{r}}\right) r^4 + 18Rr^3 + 9R^2r^2 - R^4}{9e^{\frac{2R}{r}}r^6 + (3r^2 + 3Rr + R^2)^2 r^2}, \quad (8)$$

$$V_{\text{HL}}^{(1)}(r, R) = -\frac{6(r+R) \left[3 \left(-1 + e^{\frac{2R}{r}}\right) r^3 + 6Rr^2 + 6R^2r + 2R^3\right]}{R \left[9e^{\frac{2R}{r}}r^4 + (3r^2 + 3Rr + R^2)^2\right]}, \quad (9)$$

$$\begin{aligned} V_{\text{HL}}^{(2)}(r, R) = & 3 \left[12 \left(-5 + 5e^{\frac{2R}{r}} + 6\gamma \right) r^4 + 9(-5 + 16\gamma)Rr^3 + 6(-19 + 20\gamma)R^2r^2 \right. \\ & + 2(-23 + 24\gamma)R^3r + 4(-1 + 2\gamma)R^4 + 8e^{\frac{4R}{r}} (3r^2 - 3Rr + R^2)^2 \text{Ei} \left(-\frac{4R}{r} \right) \\ & \left. - 16e^{\frac{2R}{r}} (9r^4 - 3R^2r^2 + R^4) \text{Ei} \left(-\frac{2R}{r} \right) + 8 (3r^2 + 3Rr + R^2)^2 \log \left(\frac{R}{r} \right) \right] \\ & \times \left\{ 20R \left[9e^{\frac{2R}{r}} r^4 + (3r^2 + 3Rr + R^2)^2 \right] \right\}^{-1}. \quad (10) \end{aligned}$$

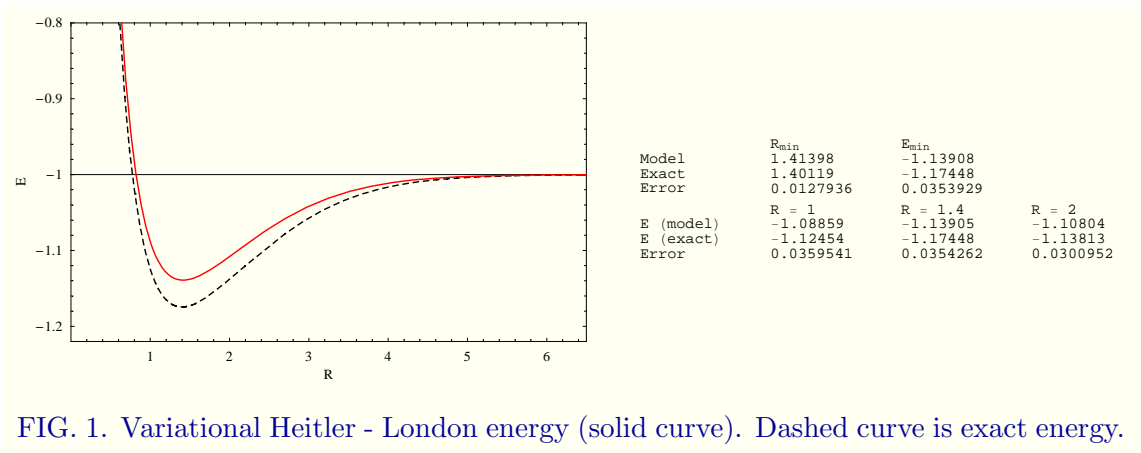


FIG. 1. Variational Heitler - London energy (solid curve). Dashed curve is exact energy.

Numerical results of minimization for different distances R are shown on Figure 1.

III. BOHR MODEL

In the nearest-atom quantization scheme, the kinetic energy of the electrons is replaced by $1/2/r_{a1}^2 + 1/2/r_{b2}^2$. The resulting Hamiltonian has no longer derivatives,

$$H_B = \frac{1}{R} + \frac{1}{2r_{a1}^2} + \frac{1}{2r_{b2}^2} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}. \quad (11)$$

In the ground state, the energy is given by the minimum of the function H_B over coordinates of two electrons. Here we consider only symmetric and planar configurations of electrons with $r_{a1} = r_{b2} = r_a$ and $r_{a2} = r_{b1} = r_b$. Then, the distance between electrons is expressed through r_a and r_b either as $|r_a^2 - r_b^2|/R$ if two electrons are located on the same half-plane from the axis, or as $(2r_a^2 + 2r_b^2 - R^2)^{1/2}$ if they are on the opposite half-planes. We consider only the latter case. Then, the Hamiltonian is a function of just two variables r_a and r_b ,

$$W_B(r_a, r_b, R) = \frac{1}{R} + T_B(r_a) + V_B^{(1)}(r_a, r_b) + V_B^{(2)}(r_a, r_b, R), \quad (12)$$

and

$$T_B(r_a) = \frac{1}{r_a^2}, \quad (13)$$

$$V_B^{(1)}(r_a, r_b) = -2/r_a - 2/r_b, \quad (14)$$

$$V_B^{(2)}(r_a, r_b, R) = (2r_a^2 + 2r_b^2 - R^2)^{-1/2}. \quad (15)$$

The Bohr energy is defined as

$$E_B(R) = \min_{r_a, r_b} W_B(r_a, r_b, R), \quad (16)$$

where minimization is performed over variables r_a and r_b satisfying triangle inequalities $r_a + r_b < R$, $r_a + R < r_b$ and $r_b + R < r_a$. Because of the effect of collapse to the opposite nucleus, $W_B(r_a, r_b, R) \rightarrow \infty$ when $r_b \rightarrow 0$. As a result, $W_B(r_a, r_b, R)$ has no absolute minimum in respect to the variable r_b . All results are calculated for a local minimum when the local minimum exists that happens for sufficiently large separations $R > 2.77$. If $R < 2.77$, then the local minimum no longer exists because it transforms into a pair of complex-conjugate stationary points. In the latter case, only real part of the energy at one of the complex stationary points is displayed. Numerical results are shown on Figure 2.

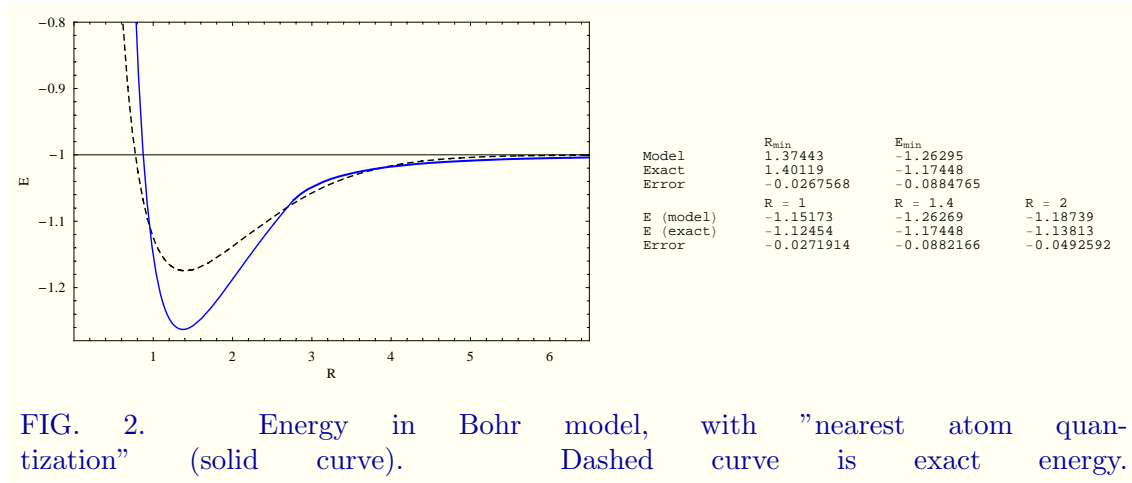


FIG. 2. Energy in Bohr model, with "nearest atom quantization" (solid curve). Dashed curve is exact energy.

IV. A HYBRID HL-B MODEL

The energy is defined as

$$E_{\text{HLB}}(R) = \min_{r_a} W_{\text{HLB}}(r_a, r_b, R), \quad (17)$$

where

$$W_{\text{HLB}}(r_a, r_b, R) = \frac{1}{R} + T_{\text{HL}}(r_a, R) + V_{\text{HL}}^{(1)}(r_a, R) + V_{\text{B}}^{(2)}(r_a, r_b, R), \quad (18)$$

and the functions T_{HL} , $V_{\text{HL}}^{(1)}$, and $V_{\text{B}}^{(2)}$ are defined by equations (8), (9), and (15) respectively. Thus, W_{HLB} is defined by the same equation (7) as the function W_{HL} , but with a replacement of the two-electron integral $V_{\text{HL}}^{(2)}(r_a, R)$ by a more simple expression for its classical analogue $V_{\text{B}}^{(2)}(r_a, r_b, R)$.

In equation (17), r_b depends on r_a , according to the constraint

$$T_{\text{HL}}(r_a, R) + V_{\text{HL}}^{(1)}(r_a, R) = T_{\text{B}}(r_a) + V_{\text{B}}^{(1)}(r_a, r_b). \quad (19)$$

Other choices of the constraint are possible, for example, $V_{\text{HL}}^{(1)}(r_a, R) = V_{\text{B}}^{(1)}(r_a, r_b)$.

Numerical results are shown on figure 3.

If we lift the constraint and instead use a minimization over two variables r_a and r_b in equation (17), then the minimal configuration would be collinear with $r_b = R + r_a$ corresponding to a minimum of the two-electron interaction $V_{\text{B}}^{(2)}(r_a, r_b, R)$ at given r_a .

If we use instead of the constraint (19) another constraint

$$-1/r_b = \Phi(r_a), \quad (20)$$

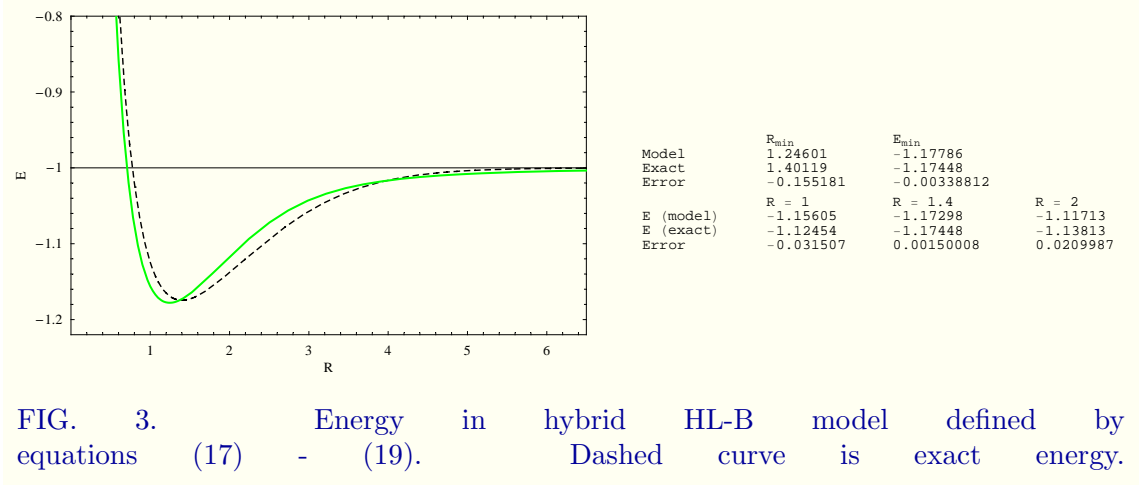


FIG. 3. Energy in hybrid HL-B model defined by equations (17) - (19). Dashed curve is exact energy.

where $\Phi(r_a)$ is given by equation (A9), as in the paper in Phys. Lett. A, then the results would be slightly less accurate, see figure 4.

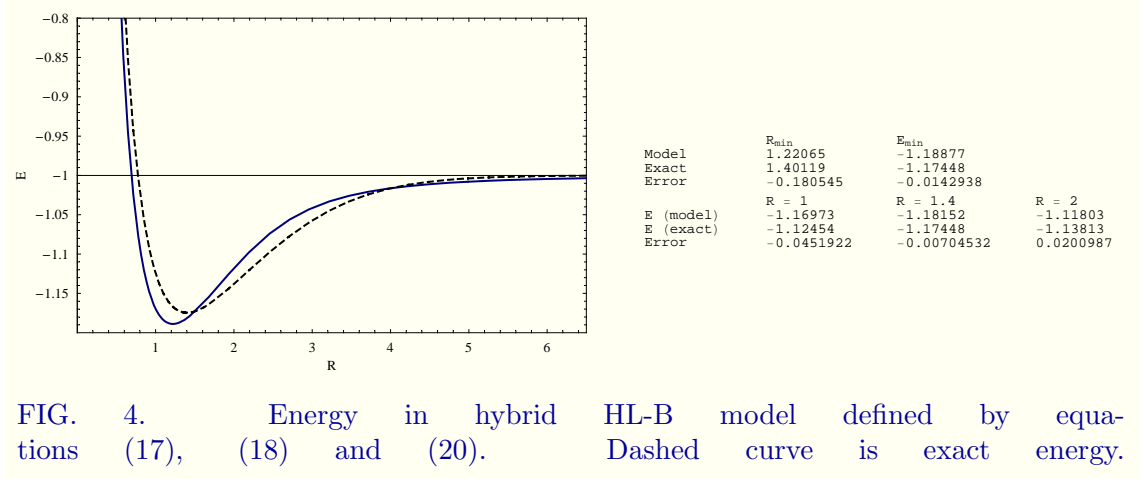


FIG. 4. Energy in hybrid HL-B model defined by equations (17), (18) and (20). Dashed curve is exact energy.

V. POSSIBLE HYBRIDS OF BOHR MODEL WITH HL MODEL

The minimization procedure given by equation (16) could be modified to prevent the effect of "collapse". Consider, for example the energy defined as

$$E_{\text{BHL}}(R) = \min_{r_a} W_{\text{B}}(r_a, r_b, R), \quad (21)$$

where the function W_{B} is given by equation (12), and r_b depends on r_a , according to the constraint

$$V_{\text{HL}}^{(1)}(r_a, R) = V_{\text{B}}^{(1)}(r_a, r_b). \quad (22)$$

In contrast to the previous section, here we minimize Bohr functional of energy instead of HL functional. Numerical results are shown on figure 5. The accuracy of this model is poor ($\simeq 0.1$).

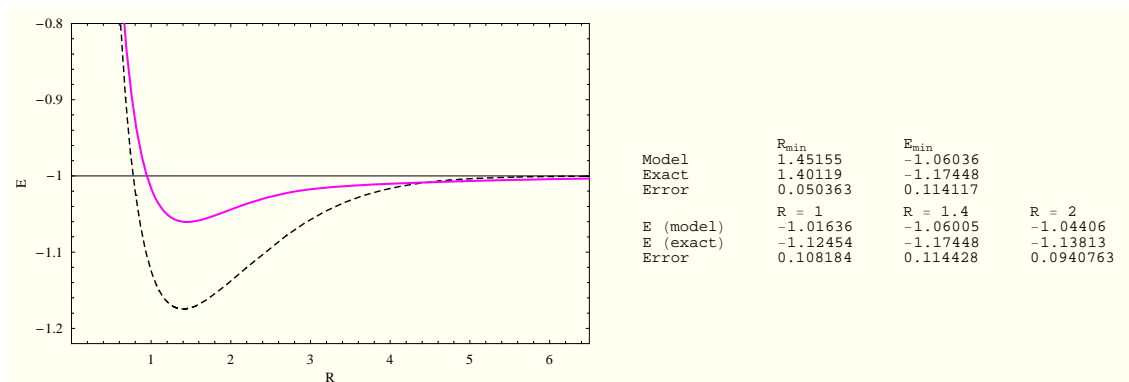


FIG. 5. Energy in hybrid BH-L model defined by equation (21) with a constraint (22). Dashed curve is exact energy.

A different choice of the constraint was used in the paper in Phys. Lett. A 355 (2006),

$$-1/r_b = \Phi(r_a, R), \quad (23)$$

where

$$\Phi(r, R) = \langle \Psi_1 | H | \Psi \rangle, \quad (24)$$

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = N(r, R) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2), \quad (25)$$

Ψ is the variational trial function (2), $N(r, R)$ is the normalization factor (3), and ψ_a and ψ_b are Slater orbitals. Numerical results for the latter constraint are shown on figure 6. In the above mentioned paper, the function Φ is in fact defined by three different ways, see Appendix A. The first and the second ways are given by equations (A2) and (A8). The results of calculations of the energy with these definitions of the function Φ are grossly inaccurate. Only the third way of definition of the function Φ given by equation (A14) or alternatively by equation (24) gives reasonable numerical results that are presented in this section.

In case of using the constraint $T_{\text{HL}}(r_a, R) + V_{\text{HL}}^{(1)}(r_a, R) = T_{\text{B}}(r_a) + V_{\text{B}}^{(1)}(r_a, r_b)$, the method is equivalent to the HL-B hybrid model described in the previous section.

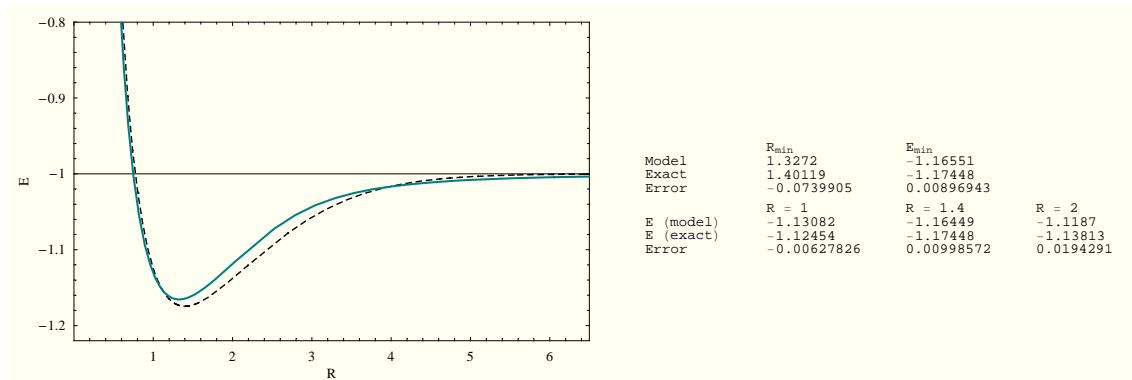


FIG. 6. Energy in hybrid B-HL model defined by equation (21) with a constraint given by equations (24) and (25). Dashed curve is exact energy.

VI. CONCLUSIONS

Variational HL functional of energy could be combined with Bohr energy in different ways. The hybrid method could give more accurate results than HL and Bohr methods by themselves considered separately. The hybrid method could be constructed by simplifying the HL functional after replacing its two-electron part by the classical energy $1/r_{12}$ or by using Bohr energy functional and imposing constraints on possible configurations to prevent the collapse. Various hybrid methods could have comparable accuracy. For multi-atomic molecules, a proper hybrid method could be chosen in order to avoid two-electron variational integrals and to decrease a number of parameters of minimization.

APPENDIX A: CHOICE OF A CONSTRAINT FROM THE PAPER IN PHYS.

LETT. A 355 (2006)

The constraint (23) was introduced in the paper of A. A. S. et al, "Model of molecular bonding based on the Bohr - Sommerfeld picture of atoms", Phys. Lett. A **355**, 373 (2006), equation (5). It was designed to prevent the effect of "collapse" on the opposite nucleus. The function $\Phi(r, R)$ has meaning of an effective potential between the electron cloud centered at nucleus A and the nuclear charge B. It is originally defined in this paper by Equation (4) as

$$\Phi(r, R) = \langle \Psi | -\frac{1}{r_{b1}} | \Psi \rangle. \quad (\text{A1})$$

This expectation value is expressed through one electron integrals in the book of Slater as

$$\Phi(r, R) = \frac{-1 + \frac{1}{2}J(R/r) + K(R/r)S(R/r)}{r [1 + S^2(R/r)]}, \quad (\text{A2})$$

where S is defined by equation (4) and

$$J(R/r) = -2r \langle \psi_a | \frac{1}{r_b} | \psi_a \rangle, \quad (\text{A3})$$

$$K(R/r) = -2r \langle \psi_a | \frac{1}{r_b} | \psi_b \rangle. \quad (\text{A4})$$

Explicitly,

$$J(w) = 2 \left[-\frac{1}{w} + e^{-2w} \left(1 + \frac{1}{w} \right) \right], \quad (\text{A5})$$

$$K(w) = -2e^{-w}(1 + w). \quad (\text{A6})$$

The function Φ is re-defined in a different way by Equation (7) of the paper as

$$\Phi(r, R) = -\frac{1}{1 + S^2(R/r)} \left(\langle \psi_a | \frac{1}{r_b} | \psi_a \rangle + 2S(R/r) \langle \psi_a | \frac{1}{r_b} | \psi_b \rangle \right), \quad (\text{A7})$$

or explicitly

$$\Phi(r, R) = \frac{\frac{1}{2}J(R/r) + K(R/r)S(R/r)}{r [1 + S^2(R/r)]}. \quad (\text{A8})$$

The expression (A8) in comparison with the expression (A2) misses one term, $-1/r/(1+S^2)$ that is equal to $\langle \Psi_1 | -1/r_{1a} | \Psi_1 \rangle$ in terms of the function (25).

The function Φ is re-defined in a third way by Equation (8) of the paper as

$$\Phi(r, R) = -\frac{1}{1 + S^2(R/r)} [f(r, R) + S(R/r)g(r, R)], \quad (\text{A9})$$

where

$$f(r, R) = \frac{1}{R} - e^{-2R/r} \left(\frac{1}{r} + \frac{1}{R} \right), \quad (\text{A10})$$

$$g(r, R) = \frac{1}{r} e^{-R/r} \left(1 + \frac{R}{r} \right). \quad (\text{A11})$$

The functions f and g are expressed through J and K as

$$f(r, R) = -\frac{J(R/r)}{2r}, \quad (\text{A12})$$

$$g(r, R) = -\frac{K(R/r)}{2r}. \quad (\text{A13})$$

Thus, equation (A9) is expressed in terms of functions J and K as

$$\Phi(r, R) = \frac{\frac{1}{2}J(R/r) + \frac{1}{2}K(R/r)S(R/r)}{r [1 + S^2(R/r)]}. \quad (\text{A14})$$

The expression (A14) has twice smaller exchange term in comparison with the expression (A8). Alternatively, it could be written as the expectation value (24).