

## I. ENERGY

The normalized wavefunction is

$$\psi(r_1, r_2) = \alpha^3 \exp(-\alpha r_1) \exp(-\alpha r_2). \quad (1)$$

Using the expression of laplacian from the previous section, the kinetic energy is

$$\langle K \rangle = -\frac{1}{2} \int \frac{\nabla_{r_1}^2 \psi}{\psi} |\psi|^2 d^3 r_1 d^3 r_2 - \frac{1}{2} \int \frac{\nabla_{r_2}^2 \psi}{\psi} |\psi|^2 d^3 r_1 d^3 r_2 \quad (2)$$

$$= -\frac{1}{2} \int_0^\infty \left( -\frac{2\alpha}{r_1} + \alpha^2 \right) \alpha^6 \exp(-2\alpha r_1) 4r_1^2 dr_1 \int_0^\infty \exp(-2\alpha r_2) 4r_2^2 dr_2 + \dots \quad (3)$$

$$= -\frac{1}{2} \left( -\frac{1}{\alpha} \right) \frac{1}{\alpha^3} \alpha^6 - \frac{1}{2} \left( -\frac{1}{\alpha} \right) \frac{1}{\alpha^3} \alpha^6 \quad (4)$$

$$= \boxed{\alpha^2}. \quad (5)$$

The electron-nuclear potential is

$$\langle V_{\text{en}} \rangle = -Z \int \frac{\alpha^6}{r_1} \exp(-2\alpha r_1) \exp(-2\alpha r_2) d^3 r_1 d^3 r_2 - \dots \quad (6)$$

$$= -Z \int_0^\infty \frac{1}{r_1} \exp(-2\alpha r_1) 4r_1^2 dr_1 \int_0^\infty \exp(-2\alpha r_2) 4r_2^2 dr_2 - \dots \quad (7)$$

$$= -Z \left( \frac{1}{\alpha^2} \right) \left( \frac{1}{\alpha^3} \right) \alpha^6 - Z \left( \frac{1}{\alpha^2} \right) \left( \frac{1}{\alpha^3} \right) \quad (8)$$

$$= \boxed{-2Z\alpha}. \quad (9)$$

## II. GRADIENT

The (unnormalized) wavefunction is

$$\psi(r_1, r_2) = \exp(-\alpha r_1) \exp(-\alpha r_2). \quad (10)$$

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2) = \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \exp\left(\alpha\sqrt{x_2^2 + y_2^2 + z_2^2}\right). \quad (11)$$

The gradient is

$$\nabla\psi = \left[ \frac{\partial\psi}{\partial x_1}, \frac{\partial\psi}{\partial y_1}, \frac{\partial\psi}{\partial z_1}, \frac{\partial\psi}{\partial x_2}, \frac{\partial\psi}{\partial y_2}, \frac{\partial\psi}{\partial z_2} \right]^T. \quad (12)$$

Evaluate each element.

$$\frac{\partial\psi}{\partial x_1} = -\alpha \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \frac{1}{2}(x_1^2 + y_1^2 + z_1^2)^{-1/2} 2x_1 \exp\left(\alpha\sqrt{x_2^2 + y_2^2 + z_2^2}\right) = -\alpha \frac{x_1}{r_1} \psi \quad (13)$$

Thus, the gradient is

$$\boxed{\frac{\nabla\psi}{\psi} = -\alpha \left[ \frac{x_1}{r_1}, \frac{y_1}{r_1}, \frac{z_1}{r_1}, \frac{x_2}{r_2}, \frac{y_2}{r_2}, \frac{z_2}{r_2} \right]^T}. \quad (14)$$

## III. LAPLACIAN

$$\frac{\partial^2\psi}{\partial x_1^2} = -\alpha \exp\left(-\alpha\sqrt{x_2^2 + y_2^2 + z_2^2}\right) \frac{\partial}{\partial x_1} \left[ x_1 \frac{1}{\sqrt{x_1^2 + y_1^2 + z_1^2}} \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \right] \quad (15)$$

$$= -\alpha \exp\left(-\alpha\sqrt{x_2^2 + y_2^2 + z_2^2}\right) \frac{\partial}{\partial x_1} A. \quad (16)$$

$$(17)$$

$$\frac{\partial A}{\partial x_1} = \frac{1}{\sqrt{x_1^2 + y_1^2 + z_1^2}} \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \quad (18)$$

$$+ x_1 \left(-\frac{1}{2}\right) (x_1^2 + y_1^2 + z_1^2)^{-\frac{3}{2}} 2x_1 \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \quad (19)$$

$$+ x_1 \frac{1}{\sqrt{x_1^2 + y_1^2 + z_1^2}} (-\alpha) \frac{1}{2} \frac{2x_1}{\sqrt{x_1^2 + y_1^2 + z_1^2}} \exp\left(-\alpha\sqrt{x_1^2 + y_1^2 + z_1^2}\right) \quad (20)$$

$$= \left[ \frac{1}{r_1} - \frac{x_1^2}{r_1^3} - \alpha \frac{x_1^2}{r_1^2} \right] \exp(-\alpha r_1). \quad (21)$$

$$(22)$$

$$\frac{\partial^2 \psi}{\partial x_1^2} = -\alpha \exp(-\alpha r_2) \left[ \frac{1}{r_1} - \frac{x_1^2}{r_1^3} - \alpha \frac{x_1^2}{r_1^2} \right] \exp(-\alpha r_1) \quad (23)$$

$$= -\frac{\alpha}{r_1} \psi \left[ 1 - \frac{x_1^2}{r_1^2} - \alpha \frac{x_1^2}{r_1} \right]. \quad (24)$$

Thus, the laplacian is

$$\frac{\nabla^2 \psi}{\psi} = \left[ \frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2}, \frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial y_2^2} + \frac{\partial^2 \psi}{\partial z_2^2} \right] \quad (25)$$

$$= \left[ -\frac{\alpha}{r_1} \left( 3 - \frac{x_1^2 + y_1^2 + z_1^2}{r_1^2} - \alpha \frac{x_1^2 + y_1^2 + z_1^2}{r_1} \right), -\frac{\alpha}{r_2} \left( 3 - \frac{x_2^2 + y_2^2 + z_2^2}{r_2^2} - \alpha \frac{x_2^2 + y_2^2 + z_2^2}{r_2} \right) \right] \quad (26)$$

$$= \left[ -\frac{\alpha}{r_1} (2 - \alpha r_1), -\frac{\alpha}{r_2} (2 - \alpha r_2) \right] \quad (27)$$

$$= \left[ -\frac{2\alpha}{r_1} + \alpha^2, -\frac{2\alpha}{r_2} + \alpha^2 \right]. \quad (28)$$

#### IV. JASTROW

The Jastrow factor is

$$\psi(r_1, r_2) = \exp(\beta r_{12}) = \exp(\beta |r_1 - r_2|) \quad (29)$$

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2) = \exp \left[ \beta \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \right] \quad (30)$$

#### V. GRADIENT

Take the derivative.

$$\frac{\partial \psi}{\partial x_1} = \beta \frac{1}{2} [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{-1/2} 2(x_1 - x_2) \exp \left[ \beta \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \right] \quad (31)$$

$$= \beta \frac{x_1 - x_2}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} \exp \left[ \beta \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \right] \quad (32)$$

$$= \beta \frac{x_1 - x_2}{r_{12}} \exp(\beta r_{12}) \quad (33)$$

$$= \beta \frac{x_1 - x_2}{r_{12}} \psi. \quad (34)$$

The gradient is

$$\frac{\nabla \psi}{\psi} = \frac{\beta}{r_{12}} [x_1 - x_2, y_1 - y_2, z_1 - z_2, x_2 - x_1, y_2 - y_1, z_2 - z_1]^T \quad (35)$$

$$= \frac{\beta}{r_{12}} [\mathbf{r}_{12}, -\mathbf{r}_{12}]^T \quad (36)$$

$$= \boxed{\frac{\beta}{r_{12}} [1, -1]^T \mathbf{r}_{12}}. \quad (37)$$

#### VI. LAPLACIAN

Take the derivative using `sympy` to reduce pain.

$$\frac{\partial^2 \psi}{\partial x_1^2} = \beta \left[ \frac{\beta (x_1 - x_2)^2}{r_{12}^2} - \frac{(x_1 - x_2)^2}{r_{12}^3} + \frac{1}{r_{12}} \right] \psi \quad (38)$$

Thus, the laplacian is

$$\frac{\nabla^2 \psi}{\psi} = \frac{\beta}{r_{12}} \left[ \frac{\beta(x_1 - x_2)^2}{r_{12}} - \frac{(x_1 - x_2)^2}{r_{12}^2} + 1 + \frac{\beta(y_1 - y_2)^2}{r_{12}} - \frac{(y_1 - y_2)^2}{r_{12}^2} + 1 + \frac{\beta(z_1 - z_2)^2}{r_{12}} - \frac{(z_1 - z_2)^2}{r_{12}^2} + 1, \right. \quad (39)$$

$$\left. \frac{\beta(x_2 - x_1)^2}{r_{12}} - \frac{(x_2 - x_1)^2}{r_{12}^2} + 1 + \frac{\beta(y_2 - y_1)^2}{r_{12}} - \frac{(y_2 - y_1)^2}{r_{12}^2} + 1 + \frac{\beta(z_2 - z_1)^2}{r_{12}} - \frac{(z_2 - z_1)^2}{r_{12}^2} + 1 \right]^T \quad (40)$$

$$= \frac{\beta}{r_{12}^2} \left[ \frac{\beta r_{12}^2}{r_{12}} - \frac{r_{12}^2}{r_{12}^2} + 3, \frac{\beta r_{12}^2}{r_{12}} - \frac{r_{12}^2}{r_{12}^2} + 3 \right]^T \quad (41)$$

$$= \frac{\beta}{r_{12}^2} [\beta r_{12} + 2, \beta r_{12} + 2]^T \quad (42)$$

$$= \boxed{\left( \frac{\beta^2}{r_{12}} + \frac{2\beta}{r_{12}^2} \right) [1, 1]^T}. \quad (43)$$