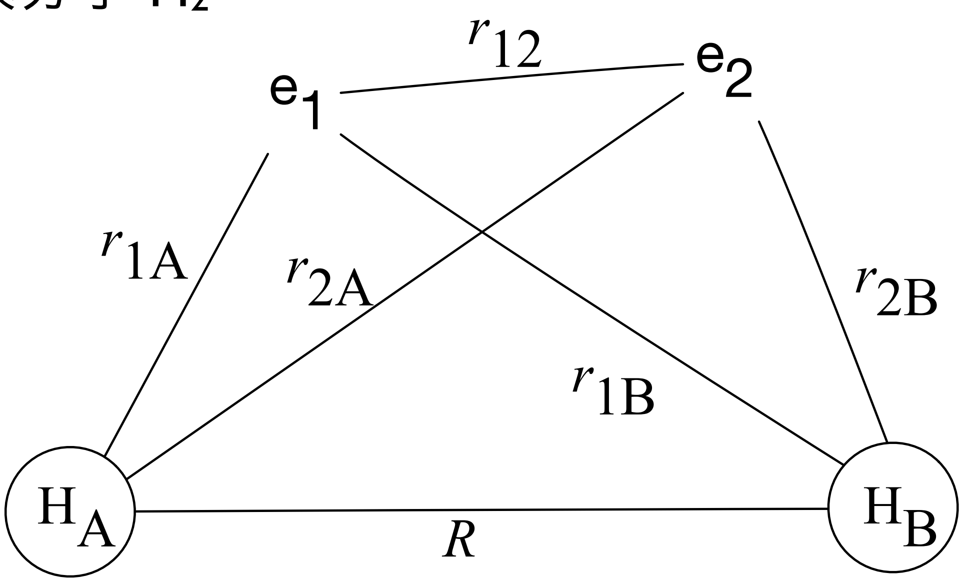
水素分子 H_2



Born-Oppenheimer approximation

$$M = m_{\mathrm{H}} >> m_{\mathrm{e}}$$ 1836倍

$$-\frac{\hbar^2}{2M}(\nabla_{\mathrm{A}}^2 + \nabla_{\mathrm{B}}^2) \to 0$$ と近似する

原子単位系 atomic unit (au)

ボーア半径 $$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_{\mathrm{e}}e^2} = 5.291772086 \times 10^{-11}\ \mathrm{m}$$

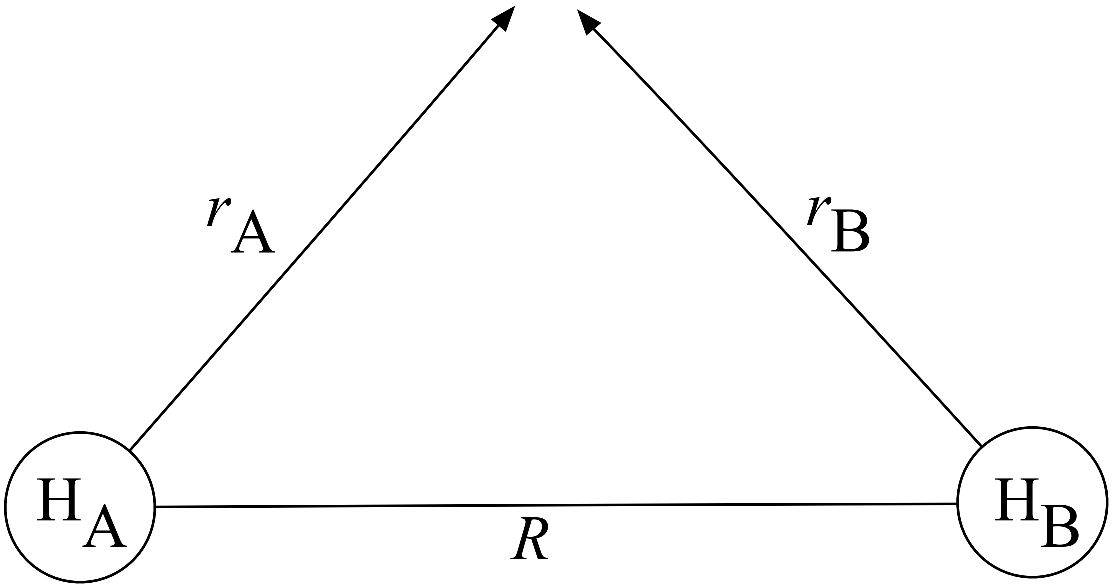
$$\to 1\ \mathrm{au}$$

$$m_{\mathrm{e}} = e = \hbar = 4\pi\epsilon_0 \to 1\ \mathrm{au}$$

$$E_{\mathrm{h}} = \frac{m_{\mathrm{e}}e^4}{(4\pi\epsilon_0)^2\hbar^2} = 4.3594 \times 10^{-18}\ \mathrm{J} = 27.211\ \mathrm{eV}$$

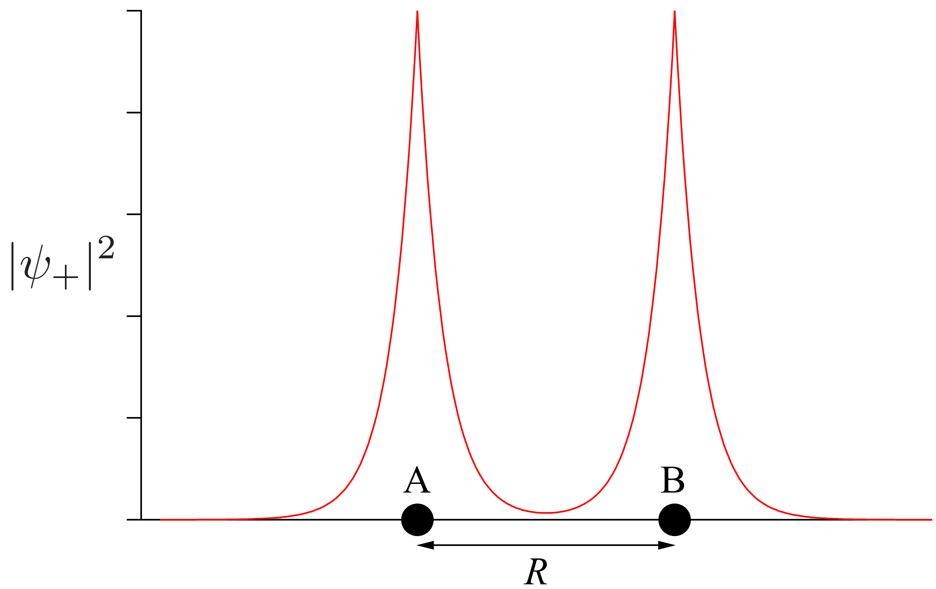
$$\to 1\ \mathrm{au}$$

水素分子カチオン H_2^+



$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}$$

$$\hat{H}\psi_j(r_\mathrm{A}, r_\mathrm{B}; R) = E_j\psi_j(r_\mathrm{A}, r_\mathrm{B}; R)$$



$$\psi_\pm = c_1 1s_\mathrm{A} \pm c_2 1s_\mathrm{B}$$

LCAO: Linear Comination of Atomic Oribitals

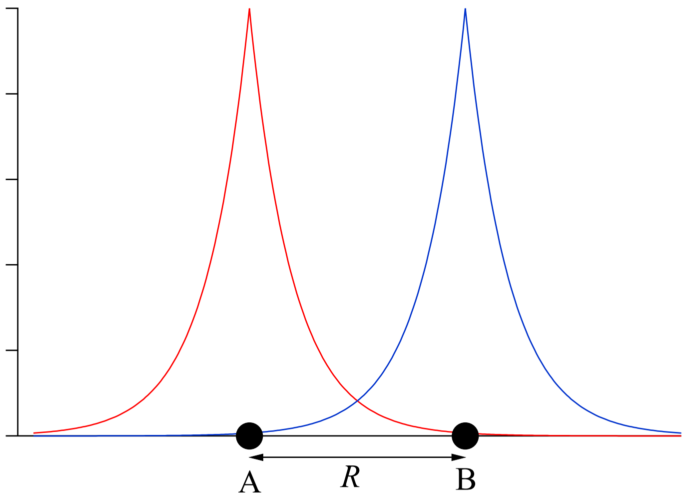
原子軌道の線形結合（一次結合）

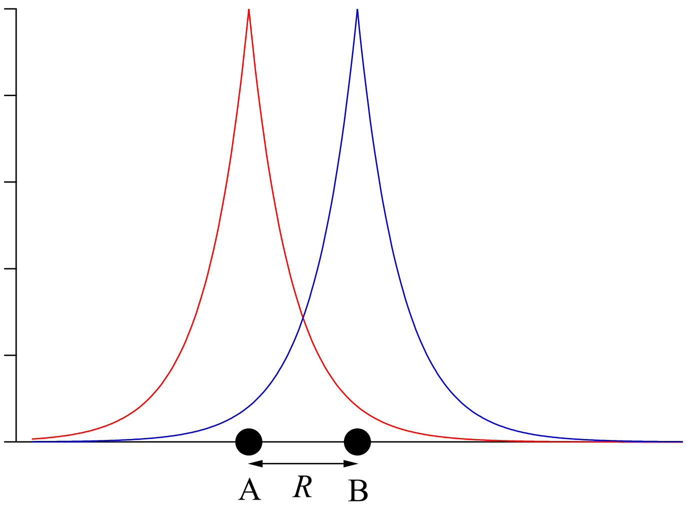
$$E_{\psi_+} = \frac{\int d\mathbf{r}\psi_+^* \hat{H} \psi_+}{\int d\mathbf{r}\psi_+^* \psi_+}$$

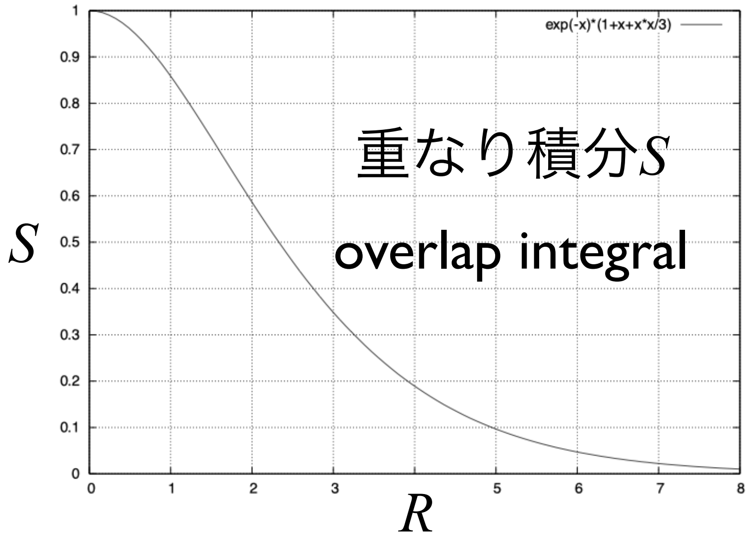
$$\begin{aligned}
\int d\mathbf{r}\psi_+^*\psi_+ &= \int d\mathbf{r}(c_1^* 1s_\mathrm{A}^* + c_2^* 1s_\mathrm{B}^*)(c_1 1s_\mathrm{A} + c_2 1s_\mathrm{B}) \\
&= |c_1|^2 \underbrace{\int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{A}}_{=1} + |c_2|^2 \underbrace{\int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{B}}_{=1} \\
&+ c_1^* c_2 \int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{B} + c_2^* c_1 \int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{A} \\
&= 2c^2 + 2c^2 S = c^2(2 + 2S) = 1 \\
S &\equiv \int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{B} = \int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{A} = \int d\mathbf{r} 1s_\mathrm{A} 1s_\mathrm{B} \\
c &\equiv c_1 = c_2 \\
c &= \frac{1}{\sqrt{2(1+S)}}
\end{aligned}$$

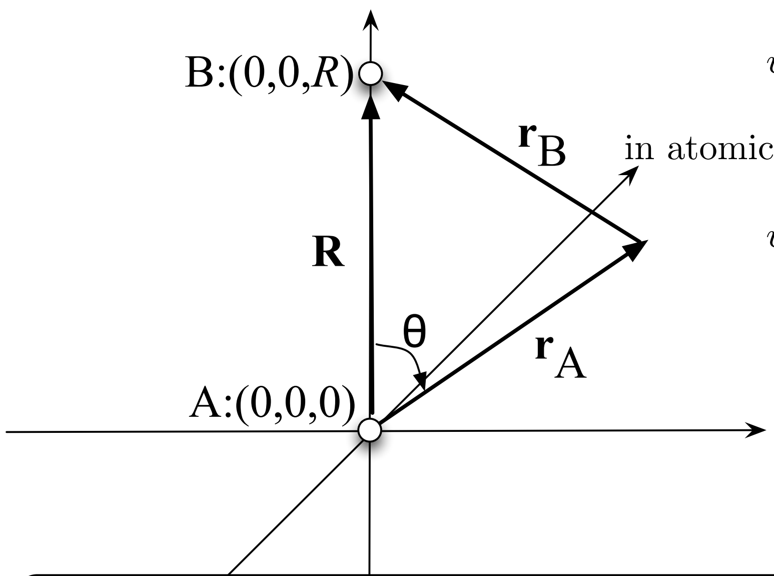
$$E_{\psi_-} = \frac{\int d\mathbf{r}\psi_-^* \hat{H} \psi_-}{\int d\mathbf{r}\psi_-^* \psi_-}$$

$$\begin{aligned}
\int d\mathbf{r}\psi_-^*\psi_- &= \int d\mathbf{r}(c_1^* 1s_\mathrm{A}^* - c_2^* 1s_\mathrm{B}^*)(c_1 1s_\mathrm{A} - c_2 1s_\mathrm{B}) \\
&= |c_1|^2 \underbrace{\int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{A}}_{=1} + |c_2|^2 \underbrace{\int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{B}}_{=1} \\
&- c_1^* c_2 \int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{B} - c_2^* c_1 \int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{A} \\
&= 2c^2 - 2c^2 S = c^2(2 - 2S) = 1 \\
S &\equiv \int d\mathbf{r} 1s_\mathrm{A}^* 1s_\mathrm{B} = \int d\mathbf{r} 1s_\mathrm{B}^* 1s_\mathrm{A} = \int d\mathbf{r} 1s_\mathrm{A} 1s_\mathrm{B} \\
c &\equiv c_1 = c_2 \\
c &= \frac{1}{\sqrt{2(1-S)}}
\end{aligned}$$









$$\psi_{1s}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi a_0}} e^{-Zr/a_0}$$

in atomic unit $a_0 = 1$, and for hydrogen $Z = 1$

$$\psi_{1s}(\mathbf{r}) = \sqrt{\frac{1}{\pi}} e^{-r}$$

$$\mathbf{R} = \mathbf{r}_A + \mathbf{r}_B$$

$$\mathbf{r}_B = \mathbf{R} - \mathbf{r}_A$$

$$r_B^2 = (\mathbf{R} - \mathbf{r}_A)^2 = R^2 + r_A^2 - 2Rr_A \cos\theta$$

$$r_B = \sqrt{R^2 + r_A^2 - 2Rr_A \cos\theta}$$

$$S = \int d\mathbf{r} 1\mathrm{s}_{\mathrm{A}}^{*} 1\mathrm{s}_{\mathrm{B}} = \frac{1}{\pi} \int d\mathbf{r}_{\mathrm{A}} e^{-r_{\mathrm{A}}} e^{-r_{\mathrm{B}}}$$

$$= \frac{1}{\pi} \int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}}^2 e^{-r_{\mathrm{A}}} \int_0^{2\pi} d\phi \underbrace{\int_0^{\pi} d\theta \sin\theta \exp\left[-\sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}\cos\theta}\right]}_{= I_\theta(r_{\mathrm{A}})}$$

$$= 2\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}}^2 e^{-r_{\mathrm{A}}} I_\theta(r_{\mathrm{A}})$$

$$I_\theta(r_{\mathrm{A}}) = \int_0^{\pi} d\theta \sin\theta \exp\left[-\sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}\cos\theta}\right]$$

$$\frac{d\cos\theta}{d\theta} = -\sin\theta,\ \cos\theta = x,\ dx = -\sin\theta d\theta$$

$$I_\theta(r_{\mathrm{A}}) = \int_{-1}^{1} dx \exp\left[-\sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}x}\right]$$

$$u = \sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}x}$$

$$\frac{du}{dx} = \frac{1}{2}(-)^{-1/2}(-2r_{\mathrm{A}}R),\ dx = -\frac{udu}{r_{\mathrm{A}}R}$$

$$x = 1; u = |r_{\mathrm{A}} - R|,\ x = -1; u = r_{\mathrm{A}} + R$$

$$I_\theta(r_{\mathrm{A}}) = \frac{1}{r_{\mathrm{A}}R} \int_{|r_{\mathrm{A}}-R|}^{r_{\mathrm{A}}+R} ue^{-u} du = \begin{cases} \frac{1}{r_{\mathrm{A}}R} \int_{R-r_{\mathrm{A}}}^{r_{\mathrm{A}}+R} ue^{-u} du,\ R > r_{\mathrm{A}} \\ \frac{1}{r_{\mathrm{A}}R} \int_{r_{\mathrm{A}}-R}^{r_{\mathrm{A}}+R} ue^{-u} du,\ R < r_{\mathrm{A}} \end{cases}$$

$$(fg)' = f'g + fg',\ fg = \int f'g + \int fg'$$

$$\int f'g = fg - \int fg'$$

$$f' = e^{ax},\ f = \frac{e^{ax}}{a},\ g = x$$

$$\int xe^{ax}dx = [\frac{e^{ax}}{a}x] - \int \frac{e^{ax}}{a}1dx = [\frac{e^{ax}}{a}x - \frac{e^{ax}}{a^2}]$$

$$= \frac{e^{ax}}{a^2}(ax-1)$$

$$\int x^2e^{ax}dx = [\frac{e^{ax}}{a}x^2] - \int \frac{e^{ax}}{a}(2x)dx$$

$$= [\frac{e^{ax}}{a}x^2] - \frac{2}{a}\int xe^{ax}dx$$

$$= [\frac{e^{ax}}{a}x^2] - \frac{2}{a}[\frac{e^{ax}}{a^2}(ax-1)]$$

$$= \left[e^{ax}(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3})\right]$$

$R > r_{\mathrm{A}}$

$$I_\theta(r_{\mathrm{A}}) = \frac{1}{r_{\mathrm{A}}R}\int_{R-r_{\mathrm{A}}}^{r_{\mathrm{A}}+R} ue^{-u}du$$

$$= -\frac{1}{r_{\mathrm{A}}R}\left[e^{-u}(u+1)\right]_{R-r_{\mathrm{A}}}^{r_{\mathrm{A}}+R}$$

$$= \frac{1}{r_{\mathrm{A}}R}[-e^{-(R+r_{\mathrm{A}})}(R+r_{\mathrm{A}}+1) + e^{-(R-r_{\mathrm{A}})}(R-r_{\mathrm{A}}+1)]$$

$R < r_{\mathrm{A}}$

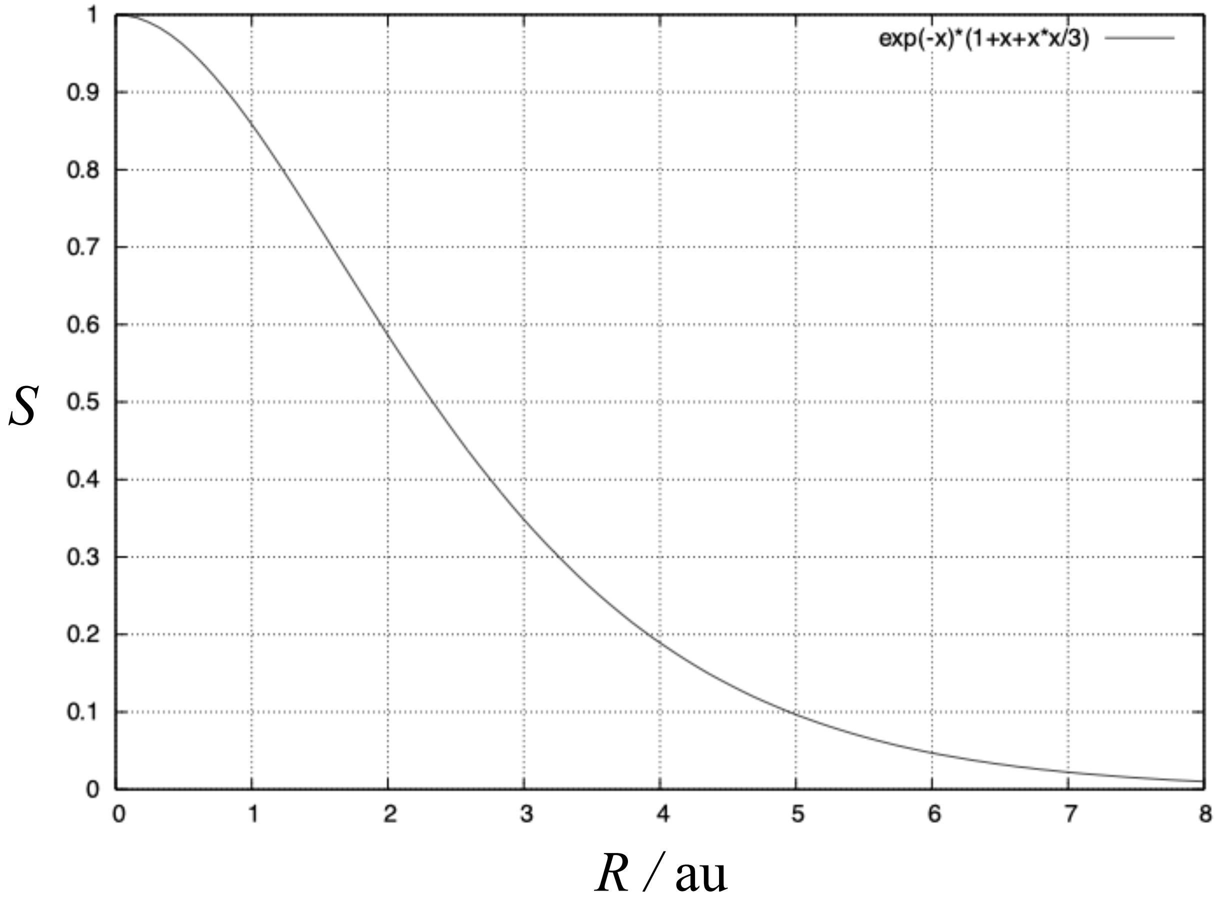
$$I_\theta(r_{\mathrm{A}}) = \frac{1}{r_{\mathrm{A}}R}\int_{r_{\mathrm{A}}-R}^{r_{\mathrm{A}}+R} ue^{-u}du$$

$$= -\frac{1}{r_{\mathrm{A}}R}\left[e^{-u}(u+1)\right]_{r_{\mathrm{A}}-R}^{r_{\mathrm{A}}+R}$$

$$= \frac{1}{r_{\mathrm{A}}R}[-e^{-(R+r_{\mathrm{A}})}(R+r_{\mathrm{A}}+1) + e^{-(r_{\mathrm{A}}-R)}(r_{\mathrm{A}}-R+1)]$$

$$
\begin{aligned}
S(R) =&2\int_0^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-r_\mathrm{A}} I_\theta(r_\mathrm{A})\\
=&2\int_0^R dr_\mathrm{A} r_\mathrm{A}^2 e^{-r_\mathrm{A}} I_\theta(r_\mathrm{A}(<R)) + 2\int_R^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-r_\mathrm{A}} I_\theta(r_\mathrm{A}(>R))\\
=&2\int_0^R dr_\mathrm{A} r_\mathrm{A}^2 e^{-r_\mathrm{A}} \frac{1}{r_\mathrm{A}R}[-e^{-(R+r_\mathrm{A})}(R+r_\mathrm{A}+1)+e^{-(R-r_\mathrm{A})}(R-r_\mathrm{A}+1)]\\
&+2\int_R^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-r_\mathrm{A}} \frac{1}{r_\mathrm{A}R}[-e^{-(R+r_\mathrm{A})}(R+r_\mathrm{A}+1)+e^{-(r_\mathrm{A}-R)}(r_\mathrm{A}-R+1)]\\
=&\frac{2e^{-R}}{R}\int_0^R dr_\mathrm{A} r_\mathrm{A} e^{-r_\mathrm{A}}[-e^{-r_\mathrm{A}}(R+r_\mathrm{A}+1)+e^{r_\mathrm{A}}(R-r_\mathrm{A}+1)]\\
&+\frac{2e^{-R}}{R}\int_R^\infty dr_\mathrm{A} r_\mathrm{A} e^{-r_\mathrm{A}}[-e^{-r_\mathrm{A}}(R+r_\mathrm{A}+1)+e^{-(r_\mathrm{A}-2R)}(r_\mathrm{A}-R+1)]\\
=&-\frac{2e^{-R}}{R}\int_0^\infty dr_\mathrm{A} r_\mathrm{A} e^{-2r_\mathrm{A}}(R+r_\mathrm{A}+1)+\frac{2e^{-R}}{R}\int_0^R dr_\mathrm{A} r_\mathrm{A}(R-r_\mathrm{A}+1)\\
&+\frac{2e^{R}}{R}\int_R^\infty dr_\mathrm{A} r_\mathrm{A} e^{-2r_\mathrm{A}}(r_\mathrm{A}-R+1)
\end{aligned}
$$

$$
\begin{aligned}
S(R) =&-\frac{2e^{-R}}{R}(R+1)\int_0^\infty dx x e^{-2x} - \frac{2e^{-R}}{R}\int_0^\infty dx x^2 e^{-2x}\\
&+\frac{2e^{-R}}{R}(R+1)\int_0^R dx x - \frac{2e^{-R}}{R}\int_0^R dx x^2\\
&+\frac{2e^{R}}{R}\int_R^\infty dx x^2 e^{-2x} + \frac{2e^{R}}{R}(1-R)\int_R^\infty dx x e^{-2x}\\
=&-\frac{2e^{-R}}{R}(R+1)\left[\frac{e^{-2x}}{4}(-2x-1)\right]_0^\infty - \frac{2e^{-R}}{R}\left[e^{-2x}(-\frac{x^2}{2}-\frac{x}{2}-\frac{1}{4})\right]_0^\infty\\
&+\frac{2e^{-R}}{R}(R+1)\left[\frac{x^2}{2}\right]_0^R - \frac{2e^{-R}}{R}\left[\frac{x^3}{3}\right]_0^R\\
&+\frac{2e^{R}}{R}\left[e^{-2x}(-\frac{x^2}{2}-\frac{x}{2}-\frac{1}{4})\right]_R^\infty + \frac{2e^{R}}{R}(1-R)\left[\frac{e^{-2x}}{4}(-2x-1)\right]_R^\infty\\
=&-\frac{e^{-R}}{2R}(R+1) - \frac{e^{-R}}{2R} + \frac{e^{-R}}{R}(R+1)R^2 - \frac{2e^{-R}}{R}\frac{R^3}{3}\\
&+\frac{2e^{R}}{R}e^{-2R}(\frac{R^2}{2}+\frac{R}{2}+\frac{1}{4}) + \frac{2e^{R}}{R}(1-R)\frac{e^{-2R}}{4}(2R+1)\\
=&e^{-R}[-\frac{1}{2}-\frac{1}{2R}-\frac{1}{2R}+R^2+R-\frac{2}{3}R^2+R+1+\frac{1}{2R}+\frac{1}{2R}(2R+1-2R^2-R)]\\
=&e^{-R}\left(1+R+\frac{1}{3}R^2\right)
\end{aligned}
$$



$$\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\hat{H}(1s_\mathrm{A} + 1s_\mathrm{B})$$
$$= c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\hat{H}1s_\mathrm{A} + c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\hat{H}1s_\mathrm{B}$$
$$= c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A}$$
$$+ c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{B}$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}}\right)1s_\mathrm{A} = E_{1s}1s_\mathrm{A}$$
$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{B}}\right)1s_\mathrm{B} = E_{1s}1s_\mathrm{B}$$

$$\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(E_{1s} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} + c^2\int d\mathbf{r}(1s_\mathrm{A}^* + 1s_\mathrm{B}^*)\left(E_{1s} - \frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B}$$

$$\frac{1}{c^2}\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = E_{1s}\underbrace{\int d\mathbf{r}(1s_\mathrm{A}^*1s_\mathrm{A} + 1s_\mathrm{B}^*1s_\mathrm{A} + 1s_\mathrm{A}^*1s_\mathrm{B} + 1s_\mathrm{B}^*1s_\mathrm{B})}_{=1+S+S+1}$$
$$+ \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} + \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A}$$
$$+ \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B} + \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{A}} + \frac{1}{R}\right)1s_\mathrm{B}$$

クーロン積分J,　交換積分K

$$J(R) = \int d\mathbf{r}1s_\mathrm{A}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} = -\int d\mathbf{r}\frac{1s_\mathrm{A}^*1s_\mathrm{A}}{r_\mathrm{B}} + \frac{1}{R}$$

$$K(R) = \int d\mathbf{r}1s_\mathrm{B}^*\left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right)1s_\mathrm{A} = -\int d\mathbf{r}\frac{1s_\mathrm{B}^*1s_\mathrm{A}}{r_\mathrm{B}} + \frac{S}{R}$$

$$\frac{1}{c^2}\int d\mathbf{r}\psi_+^*\hat{H}\psi_+ = 2E_{1s}(1+S) + 2J + 2K$$

$$E_+ = \frac{c^2[2E_{1s}(1+S) + 2J + 2K]}{2c^2(1+S)} = E_{1s} + \frac{J}{1+S} + \frac{K}{1+S}$$

$$\Delta E_+ = E_+ - E_{1s} = \frac{J}{1+S} + \frac{K}{1+S}$$

$$
\begin{aligned}
E_{\psi_-} =& \frac{\int d\mathbf{r}\psi_-^* \hat{H}\psi_-}{\int d\mathbf{r}\psi_-^*\psi_-} \\
=& c^2 \frac{\int d\mathbf{r}(1s_{\mathrm{A}}^* - 1s_{\mathrm{B}}^*)\hat{H}(1s_{\mathrm{A}} - 1s_{\mathrm{B}})}{2c^2(1-S)} \\
2(1-S)E_{\psi_-} =& \int d\mathbf{r}(1s_{\mathrm{A}}^* - 1s_{\mathrm{B}}^*)(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}} + \frac{1}{R})1s_{\mathrm{A}} \\
& - \int d\mathbf{r}(1s_{\mathrm{A}}^* - 1s_{\mathrm{B}}^*)(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}} + \frac{1}{R})1s_{\mathrm{B}} \\
=& \int d\mathbf{r}(1s_{\mathrm{A}}^* - 1s_{\mathrm{B}}^*)(E_{1s} - \frac{1}{r_{\mathrm{B}}} + \frac{1}{R})1s_{\mathrm{A}} \\
& - \int d\mathbf{r}(1s_{\mathrm{A}}^* - 1s_{\mathrm{B}}^*)(E_{1s} - \frac{1}{r_{\mathrm{A}}} + \frac{1}{R})1s_{\mathrm{B}}
\end{aligned}
$$

$$
\begin{aligned}
&\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{A}}}\right) 1s_{\mathrm{A}} = E_{1s}1s_{\mathrm{A}} \\
&\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{B}}}\right) 1s_{\mathrm{B}} = E_{1s}1s_{\mathrm{B}}
\end{aligned}
$$

$$
\begin{aligned}
2(1-S)E_{\psi_-} =& E_{1s} \underbrace{\int d\mathbf{r}(1s_{\mathrm{A}}^*1s_{\mathrm{A}} - 1s_{\mathrm{B}}^*1s_{\mathrm{A}} - 1s_{\mathrm{A}}^*1s_{\mathrm{B}} + 1s_{\mathrm{B}}^*1s_{\mathrm{B}})}_{=1-S-S+1} \\
& + \int d\mathbf{r}1s_{\mathrm{A}}^* \left(-\frac{1}{r_{\mathrm{B}}} + \frac{1}{R}\right) 1s_{\mathrm{A}} - \int d\mathbf{r}1s_{\mathrm{B}}^* \left(-\frac{1}{r_{\mathrm{B}}} + \frac{1}{R}\right) 1s_{\mathrm{A}} \\
& - \int d\mathbf{r}1s_{\mathrm{A}}^* \left(-\frac{1}{r_{\mathrm{A}}} + \frac{1}{R}\right) 1s_{\mathrm{B}} + \int d\mathbf{r}1s_{\mathrm{B}}^* \left(-\frac{1}{r_{\mathrm{A}}} + \frac{1}{R}\right) 1s_{\mathrm{B}} \\
& = 2(1-S)E_{1s} + J - K - K + J
\end{aligned}
$$

$$
E_- = E_{\psi_-} = E_{1s} + \frac{J}{1-S} - \frac{K}{1-S}
$$

永年方程式

$$\int d\mathbf{r}\psi^* \hat{H}\psi = E\int d\mathbf{r}\psi^*\psi,\ \psi = c_1 1s_{\mathrm{A}} + c_2 1s_{\mathrm{B}}$$

$$\begin{aligned} & c_1^* c_1 H_{\mathrm{AA}} + c_1^* c_2 H_{\mathrm{AB}} + c_2^* c_1 H_{\mathrm{BA}} + c_2^* c_2 H_{\mathrm{BB}} \\ & = E(c_1^* c_1 S_{\mathrm{AA}} + c_1^* c_2 S_{\mathrm{AB}} + c_2^* c_1 S_{\mathrm{BA}} + c_2^* c_2 S_{\mathrm{BB}}) \end{aligned}$$

$$c_1 H_{\mathrm{AA}} + c_2 H_{\mathrm{AB}} = \underbrace{\frac{\partial E}{\partial c_1^*}}_{=0}(\ldots) + E(c_1 S_{\mathrm{AA}} + c_2 S_{\mathrm{AB}})$$

$$c_1 H_{\mathrm{BA}} + c_2 H_{\mathrm{BB}} = \underbrace{\frac{\partial E}{\partial c_2^*}}_{=0}(\ldots) + E(c_1 S_{\mathrm{BA}} + c_2 S_{\mathrm{BB}})$$

$$0 = \begin{pmatrix} H_{\mathrm{AA}} - ES_{\mathrm{AA}} & H_{\mathrm{AB}} - ES_{\mathrm{AB}} \\ H_{\mathrm{BA}} - ES_{\mathrm{BA}} & H_{\mathrm{BB}} - ES_{\mathrm{BB}} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$0 = \begin{vmatrix} H_{\mathrm{AA}} - ES_{\mathrm{AA}} & H_{\mathrm{AB}} - ES_{\mathrm{AB}} \\ H_{\mathrm{BA}} - ES_{\mathrm{BA}} & H_{\mathrm{BB}} - ES_{\mathrm{BB}} \end{vmatrix}$$

$$S_{\mathrm{AA}} = S_{\mathrm{BB}} = 1 = \int d\mathbf{r} 1s_{\mathrm{A}}^* 1s_{\mathrm{A}} = \int d\mathbf{r} 1s_{\mathrm{B}}^* 1s_{\mathrm{B}}$$

$$S_{\mathrm{AB}} = S_{\mathrm{BA}} = S = \int d\mathbf{r} 1s_{\mathrm{A}}^* 1s_{\mathrm{B}} = \int d\mathbf{r} 1s_{\mathrm{B}}^* 1s_{\mathrm{A}}$$

$$H_{\mathrm{AA}} = H_{\mathrm{BB}} = \int d\mathbf{r} 1s_{\mathrm{A}}^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}} + \frac{1}{R}\right) 1s_{\mathrm{A}} = E_{1s} + J$$

$$H_{\mathrm{AB}} = H_{\mathrm{BA}} = \int d\mathbf{r} 1s_{\mathrm{A}}^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}} + \frac{1}{R}\right) 1s_{\mathrm{B}} = E_{1s}S + K$$

$$0 = \begin{vmatrix} E_{1s} + J - E & E_{1s}S + K - ES \\ E_{1s}S + K - ES & E_{1s} + J - E \end{vmatrix}$$

$$0 = (E_{1s} + J - E)^2 - (E_{1s}S + K - ES)^2$$

$$E_{1s} + J - E = \pm(E_{1s}S + K - ES)$$

$$E_{1s} + J - E = E_{1s}S + K - ES, E_{1s}(1 - S) + J - K = E(1 - S)$$

$$E_{1s} + J - E = -(E_{1s}S + K - ES), E_{1s}(1 + S) + J + K = E(1 + S)$$

$$E = E_{1s} + \frac{J \pm K}{1 \pm S}$$

$$0 = (E_{1s} + J - E_+)c_{1+} + (E_{1s}S + K - E_+S)c_{2+}$$

$$c_{1+} - c_{2+} = 0$$

$$\psi_+ = c_+(1s_\mathrm{A} + 1s_\mathrm{B}),\ c_+ = \frac{1}{\sqrt{2(1+S)}}$$

$$0 = (E_{1s} + J - E_-)c_{1-} + (E_{1s}S + K - E_-S)c_{2-}$$

$$c_{1-} + c_{2-} = 0$$

$$\psi_- = c_-(1s_\mathrm{A} - 1s_\mathrm{B}),\ c_- = \frac{1}{\sqrt{2(1-S)}}$$

$$J(R) = \int d\mathbf{r} 1s_\mathrm{A}^* \left(-\frac{1}{r_\mathrm{B}} + \frac{1}{R}\right) 1s_\mathrm{A} = -\int d\mathbf{r} \frac{1s_\mathrm{A}^* 1s_\mathrm{A}}{r_\mathrm{B}} + \frac{1}{R}$$

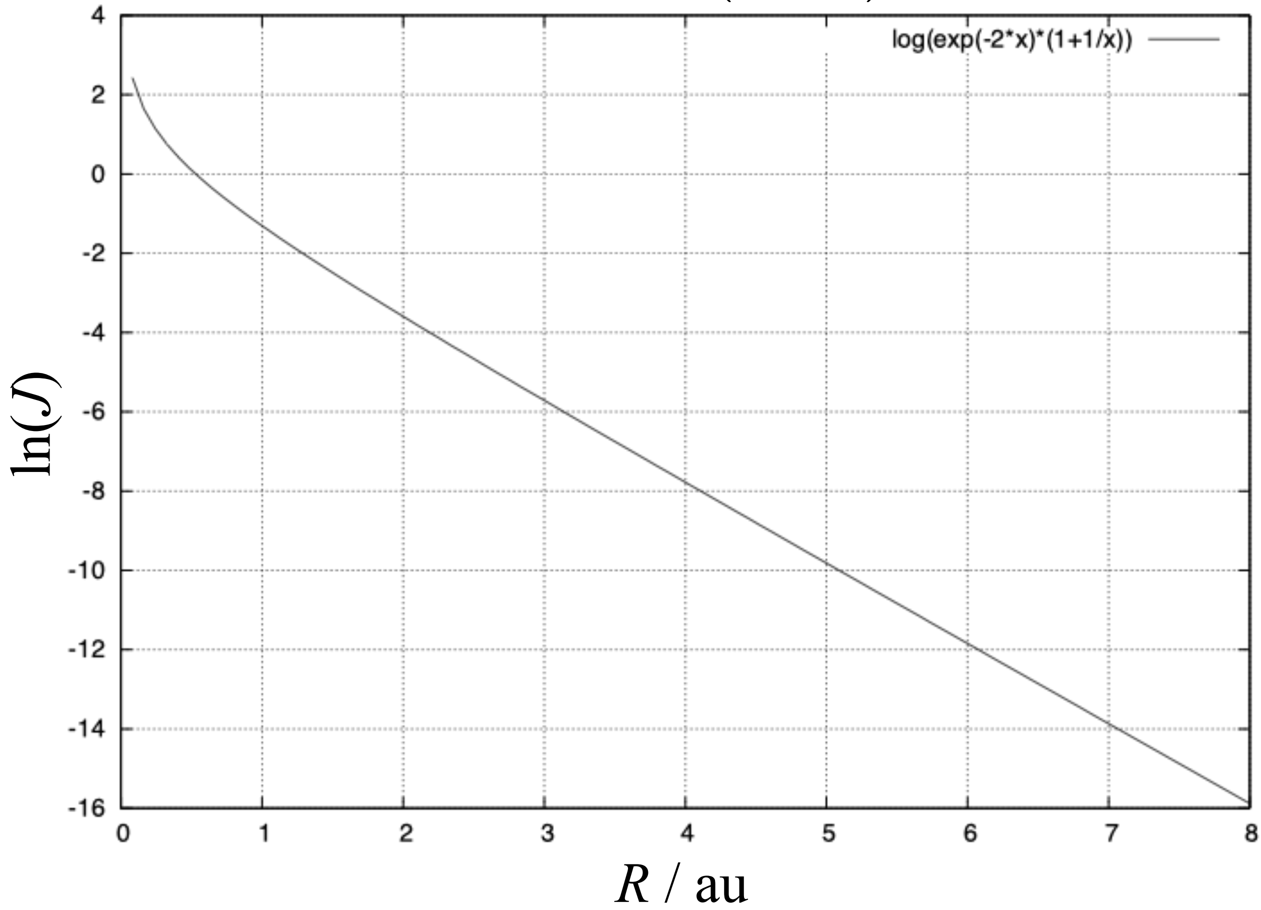
$$\begin{aligned}
J(R) =& \frac{1}{R} - \frac{1}{\pi}\int_0^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-2r_\mathrm{A}} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \frac{1}{\sqrt{R^2 + r_\mathrm{A}^2 - 2Rr_\mathrm{A}\cos\theta}} \\
=& \frac{1}{R} - 2\int_0^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-2r_\mathrm{A}} \int_{-1}^{1} dx \frac{1}{\sqrt{R^2 + r_\mathrm{A}^2 - 2Rr_\mathrm{A}x}} \\
=& \frac{1}{R} - 2\int_0^\infty dr_\mathrm{A} r_\mathrm{A}^2 e^{-2r_\mathrm{A}} \frac{1}{r_\mathrm{A}R} \int_{|r_\mathrm{A}-R|}^{r_\mathrm{A}+R} udu\frac{1}{u} \\
=& \frac{1}{R} - \frac{2}{R}\int_0^\infty dr_\mathrm{A} r_\mathrm{A} e^{-2r_\mathrm{A}} \int_{|r_\mathrm{A}-R|}^{r_\mathrm{A}+R} du \\
=& \frac{1}{R} - \frac{2}{R}\int_0^\infty dr_\mathrm{A} r_\mathrm{A} e^{-2r_\mathrm{A}} (r_\mathrm{A} + R - |r_\mathrm{A} - R|)
\end{aligned}$$

$$
\begin{aligned}
J(R) =& \frac{1}{R} - \frac{2}{R}\int_0^{\infty} dx e^{-2x} x(x+R) \\
&+ \frac{2}{R}\int_0^{R} dx e^{-2x} x(R-x) \\
&+ \frac{2}{R}\int_R^{\infty} dx e^{-2x} x(x-R) \\
=& \frac{1}{R} - \frac{2}{R}\left[e^{-2x}(-\frac{x^2}{2} - \frac{2x}{4} - \frac{2}{8})\right]_0^{\infty} - \frac{2}{R}R\left[\frac{e^{-2x}}{4}(-2x-1)\right]_0^{\infty} \\
&- \frac{2}{R}\left[e^{-2x}(-\frac{x^2}{2} - \frac{2x}{4} - \frac{2}{8})\right]_0^{R} + \frac{2}{R}R\left[\frac{e^{-2x}}{4}(-2x-1)\right]_0^{R} \\
&+ \frac{2}{R}\left[e^{-2x}(-\frac{x^2}{2} - \frac{2x}{4} - \frac{2}{8})\right]_R^{\infty} - \frac{2}{R}R\left[\frac{e^{-2x}}{4}(-2x-1)\right]_R^{R}
\end{aligned}
$$

$$
\begin{aligned}
J(R) &= \frac{1}{R} - \frac{2}{R}\frac{1}{4} - 2\frac{1}{4} \\
&- \frac{2}{R}[e^{-2R}(-\frac{R^2}{2} - \frac{R}{2} - \frac{1}{4}) + \frac{1}{4}] + 2[\frac{e^{-2R}}{4}(-2R-1) + \frac{1}{4}] \\
&- \frac{2}{R}[e^{-2R}(-\frac{R^2}{2} - \frac{R}{2} - \frac{1}{4})] + 2\frac{e^{-2R}}{4}(-2R-1) \\
&= \frac{1}{R} - \frac{2}{2R} - \frac{1}{2} + \frac{1}{2} + e^{-2R}(2R + 2 + \frac{1}{R}) + e^{-2R}(-2R-1) \\
&= e^{-2R}\left(1 + \frac{1}{R}\right)
\end{aligned}
$$

クーロン積分J $J(R) = e^{-2R}\left(1 + \frac{1}{R}\right)$

$$J(R) = e^{-2R}\left(1 + \frac{1}{R}\right)$$



交換積分K

$$K(R) = \int d\mathbf{r} 1s_{\mathrm{B}}^{*}\left(-\frac{1}{r_{\mathrm{B}}} + \frac{1}{R}\right)1s_{\mathrm{A}} = -\int d\mathbf{r}\frac{1s_{\mathrm{B}}^{*}1s_{\mathrm{A}}}{r_{\mathrm{B}}} + \frac{S}{R}$$

$$\begin{aligned}
K(R) - \frac{S}{R} =& -\int d\mathbf{r}\frac{1s_{\mathrm{B}}^{*}1s_{\mathrm{A}}}{r_{\mathrm{B}}} = -\frac{1}{\pi}\int d\mathbf{r}_{\mathrm{A}}\frac{e^{-r_{\mathrm{B}}}e^{-r_{\mathrm{A}}}}{r_{\mathrm{B}}} \\
=& -\frac{1}{\pi}\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}}^2 e^{-r_{\mathrm{A}}}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \frac{e^{-r_{\mathrm{B}}}}{r_{\mathrm{B}}} \\
=& -2\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}}^2 e^{-r_{\mathrm{A}}}\int_{-1}^{1} dx \frac{e^{-r_{\mathrm{B}}}}{r_{\mathrm{B}}}
\end{aligned}$$

$$r_{\mathrm{B}} = \sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}\cos\theta},\ x = \cos\theta,\ dx = -\sin\theta d\theta$$

$$u = \sqrt{R^2 + r_{\mathrm{A}}^2 - 2Rr_{\mathrm{A}}x}, \frac{du}{dx} = \frac{1}{2}(...)^{-1/2}(-2Rr_{\mathrm{A}}), dx = -\frac{1}{Rr_{\mathrm{A}}}udu$$

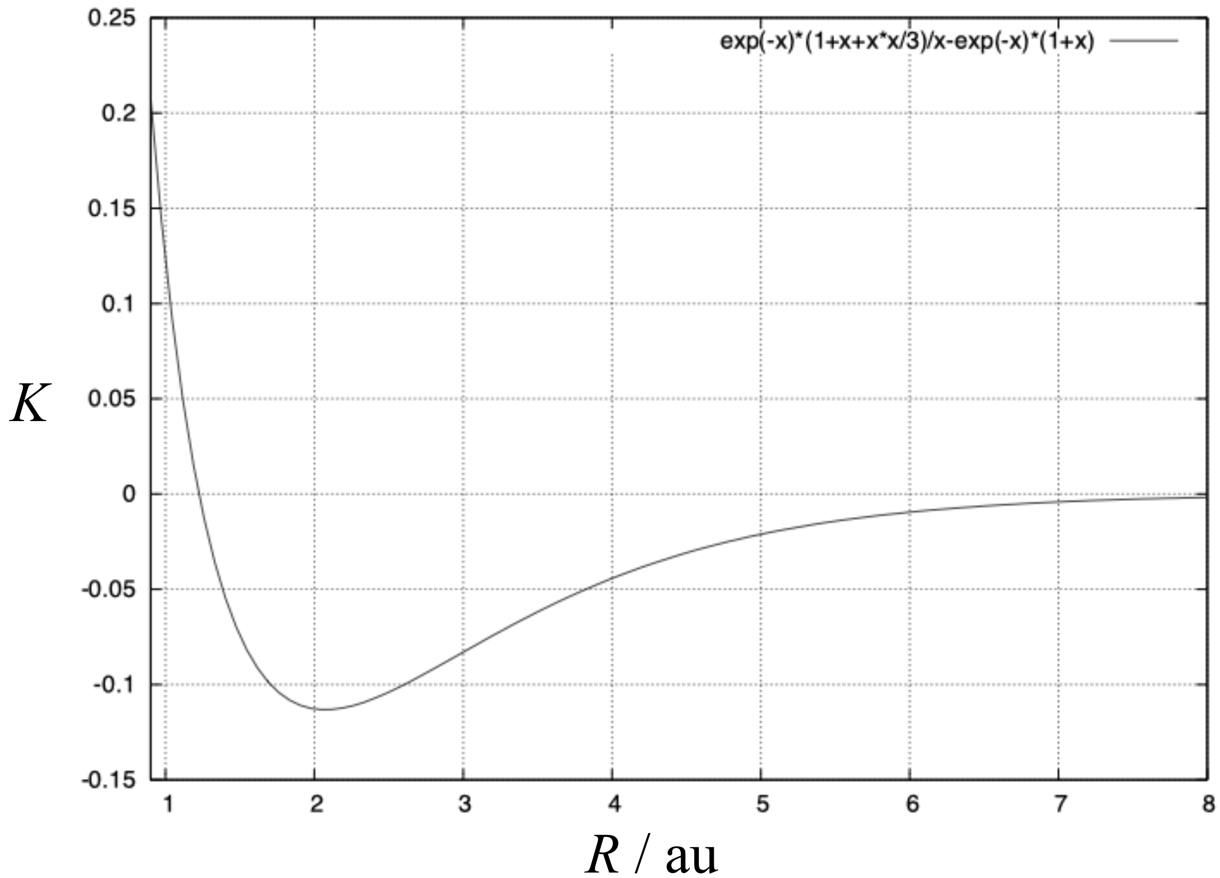
$$\begin{aligned}
K(R) - \frac{S}{R} =& -\frac{2}{R}\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}} e^{-r_{\mathrm{A}}}\int_{|r_{\mathrm{A}}-R|}^{r_{\mathrm{A}}+R} duu\frac{e^{-u}}{u} = -\frac{2}{R}\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}} e^{-r_{\mathrm{A}}}[-e^{-u}]_{|r_{\mathrm{A}}-R}^{r_{\mathrm{A}}+R} \\
=& \frac{2}{R}\int_0^{\infty} dr_{\mathrm{A}} r_{\mathrm{A}} e^{-r_{\mathrm{A}}}(e^{-(r_{\mathrm{A}}+R)} - e^{-|r_{\mathrm{A}}-R|})
\end{aligned}$$

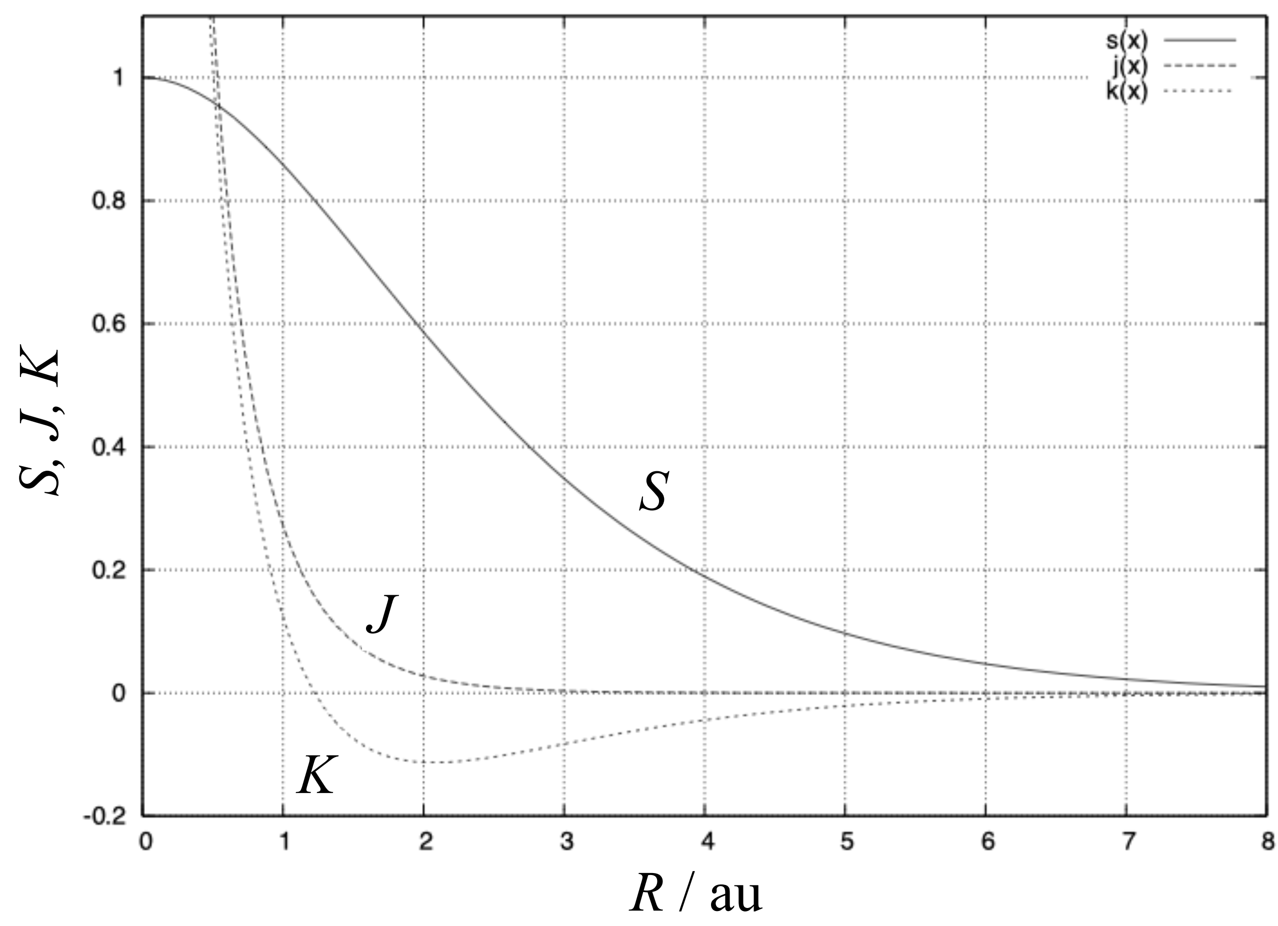
$$
\begin{aligned}
K(R) - \frac{S}{R} =& \frac{2}{R}\int_0^\infty dr_\mathrm{A} r_\mathrm{A} e^{-r_\mathrm{A}}(e^{-(r_\mathrm{A}+R)} - e^{-|r_\mathrm{A}-R|}) \\
=& \frac{2e^{-R}}{R}\int_0^\infty dx x e^{-2x} \\
& - \frac{2}{R}\int_0^R dx x e^{-x} e^{-(R-x)} - \frac{2}{R}\int_R^\infty dx x e^{-x} e^{-(x-R)} \\
=& \frac{2e^{-R}}{R}[\frac{e^{-2x}}{4}(-2x-1)]_0^\infty - \frac{2e^{-R}}{R}\frac{R^2}{2} - \frac{2e^{R}}{R}[\frac{e^{-2x}}{4}(-2x-1)]_R^\infty \\
=& \frac{2e^{-R}}{R}\frac{1}{4} - Re^{-R} - \frac{2e^{R}}{R}[-\frac{e^{-2R}}{4}(-2R-1)] \\
=& e^{-R}(\frac{1}{2R} - R - 1 - \frac{1}{2R}) \\
=& -e^{-R}(R+1)
\end{aligned}
$$

$$
K(R) = \frac{S(R)}{R} - e^{-R}(1+R)
$$

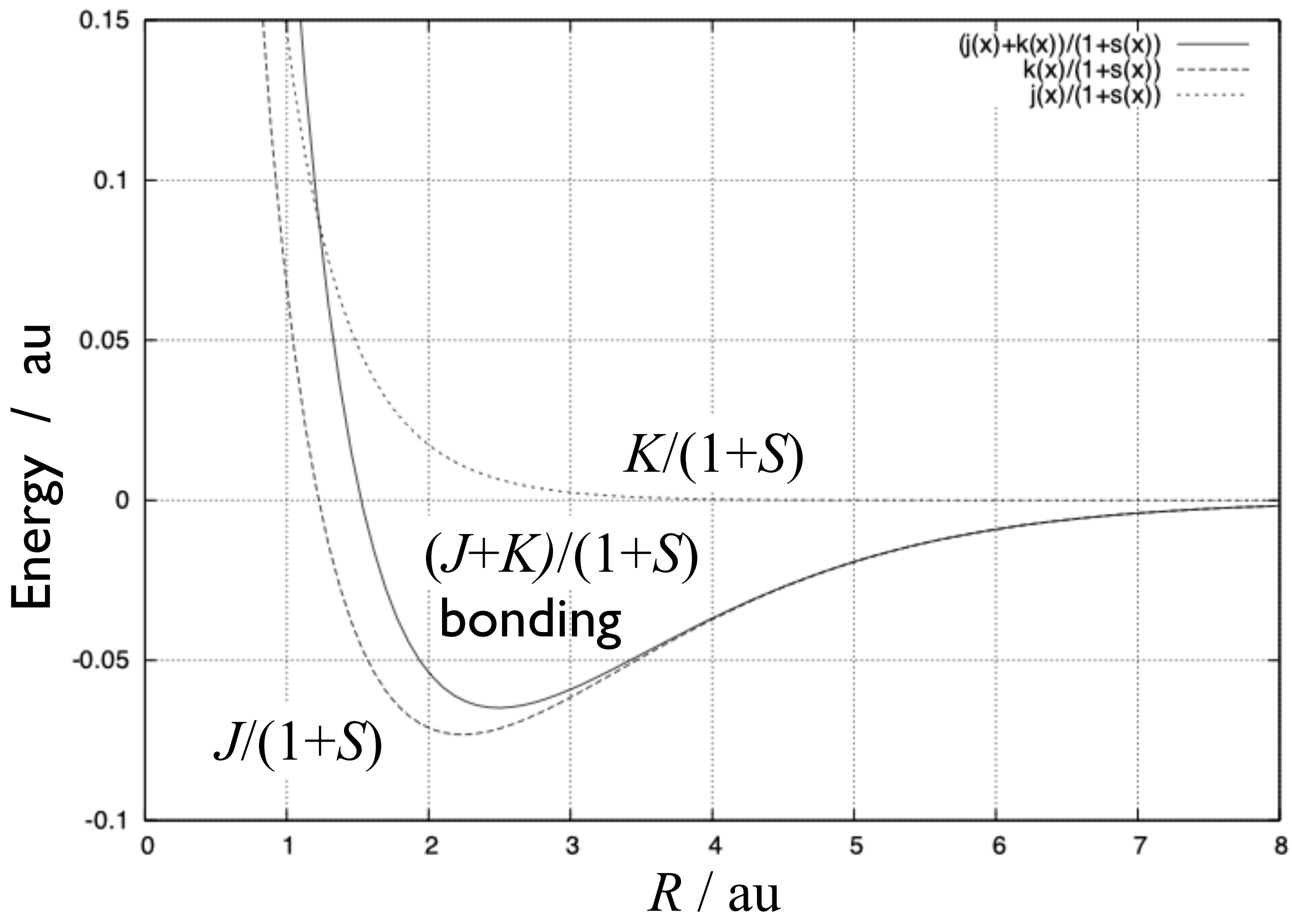
交換積分K

$$
K(R) = \frac{S}{R} - e^{-R}(1+R)
$$

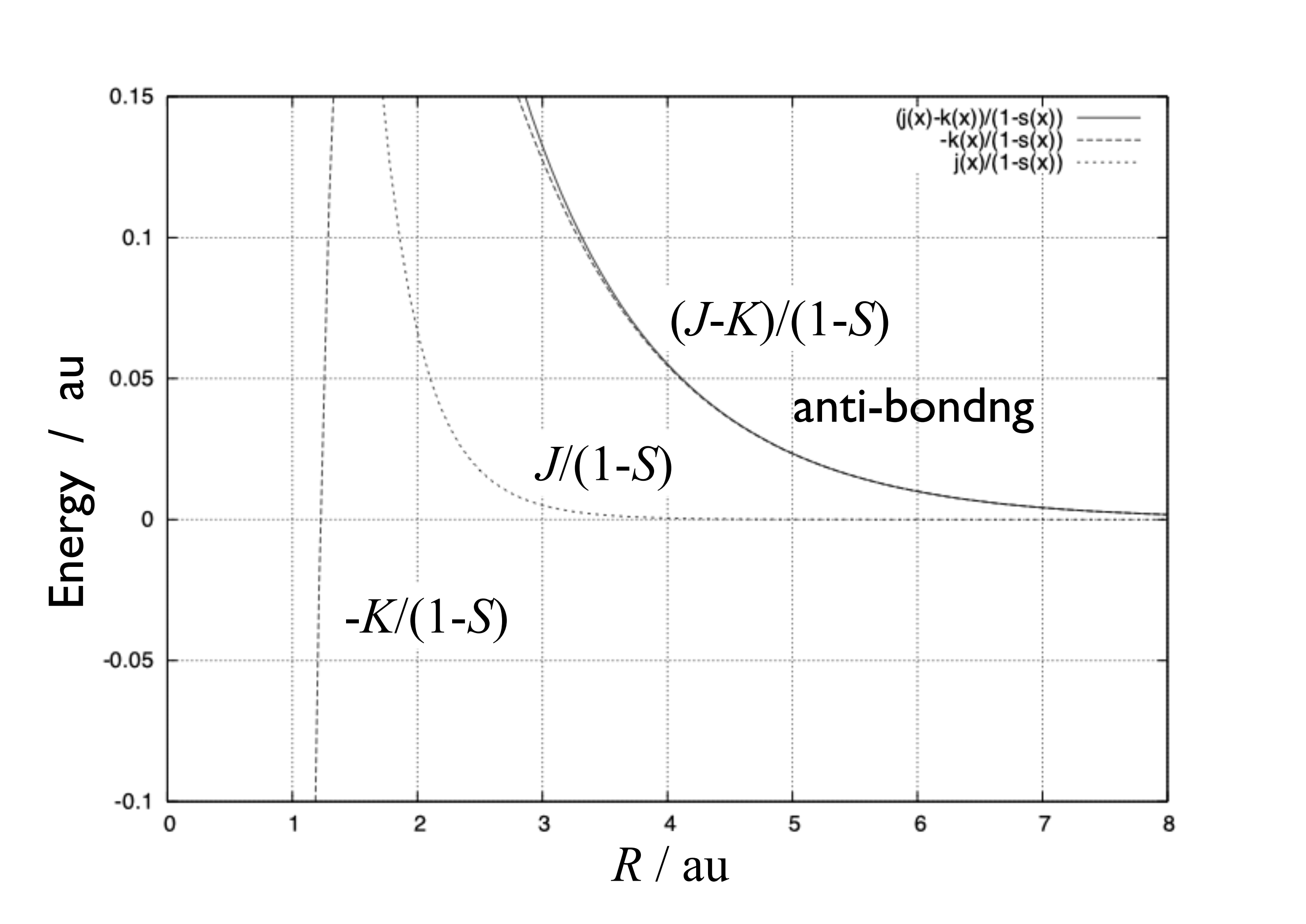




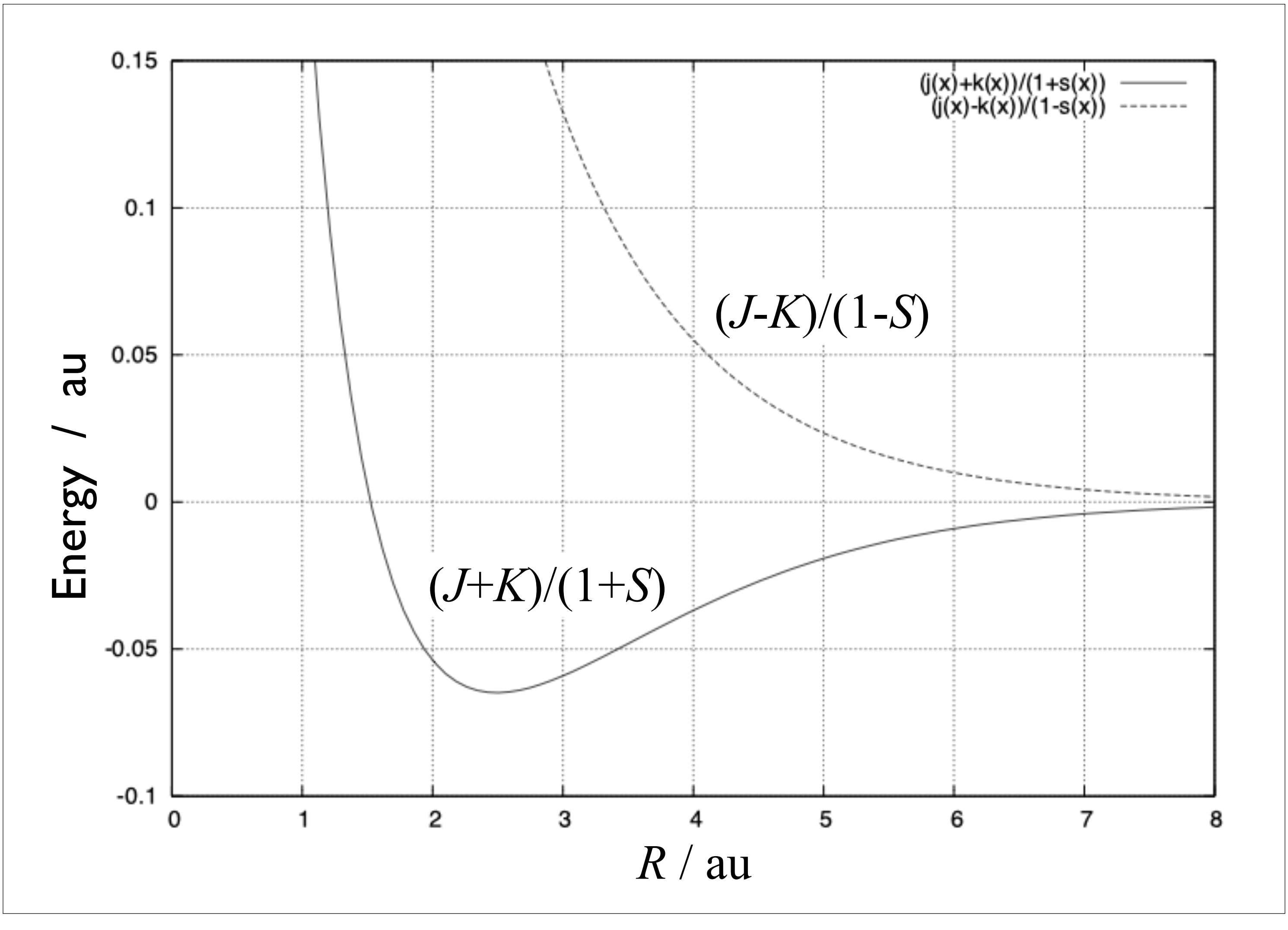
s(x)
j(x)
k(x)
S, J, K
S
J
K
R / au
1
0.8
0.6
0.4
0.2
0
-0.2
0
1
2
3
4
5
6
7
8



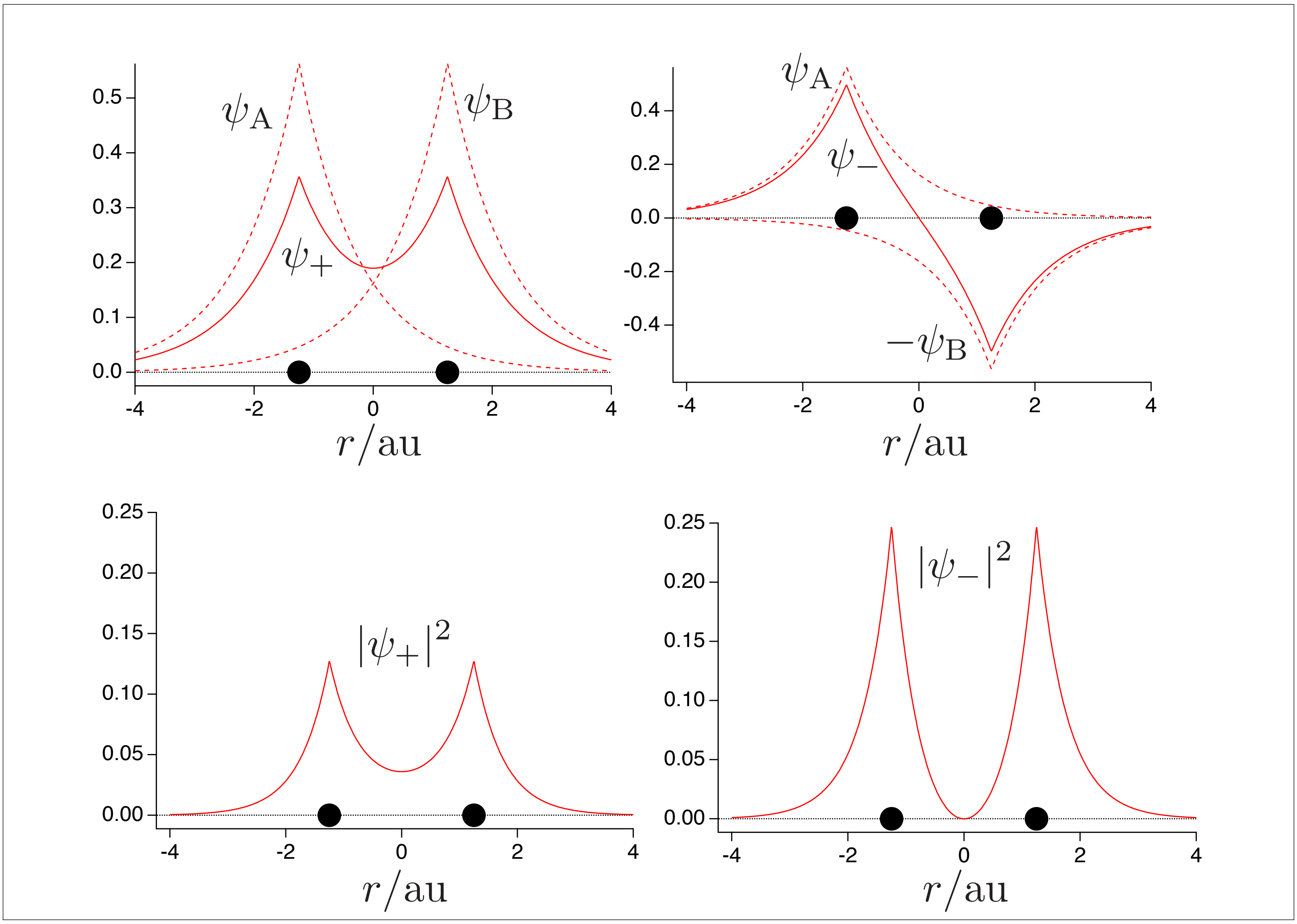
(j(x)+k(x))/(1+s(x))
k(x)/(1+s(x))
j(x)/(1+s(x))
Energy / au
K/(1+S)
(J+K)/(1+S)
bonding
J/(1+S)
R / au
0.15
0.1
0.05
0
-0.05
-0.1
0
1
2
3
4
5
6
7
8



(j(x)-k(x))/(1-s(x))
-k(x)/(1-s(x))
j(x)/(1-s(x))
(J-K)/(1-S)
anti-bondng
J/(1-S)
-K/(1-S)
Energy / au
R / au



(j(x)+k(x))/(1+s(x))
(j(x)-k(x))/(1-s(x))
(J-K)/(1-S)
(J+K)/(1+S)
Energy / au
R / au



ψ_A
ψ_B
ψ_+
$r/$au
ψ_A
ψ_-
$-\psi_B$
$r/$au
$|\psi_+|^2$
$r/$au
$|\psi_-|^2$
$r/$au