Quantum Mechanics - HW18

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7.8

$$\psi_0(\boldsymbol{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

$$D \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle$$

$$X \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle$$

First, finding D,

$$D = a \int \psi_0^*(r_1) \frac{1}{r_2} \psi_0(r_1) d^3\boldsymbol{r}$$

$$D = a \int \frac{1}{\pi a^3} \frac{1}{r_2} e^{-2r_1/a} d^3\boldsymbol{r} = \frac{1}{\pi a^2} \int \frac{1}{r_2} e^{-2r_1/a} d^3\boldsymbol{r}$$

$$r_1 = \sqrt{r^2 + R^2 - 2rR\cos\theta} \qquad r_2 = r$$

$$D = \frac{1}{\pi a^2} \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} \frac{1}{r_2} e^{-2r_1/a} dr d\theta d\phi$$

$$D = \frac{1}{\pi a^2} \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} \frac{1}{r} e^{-2\sqrt{r^2+R^2-2rR\cos\theta}/a} r^2 \sin\theta dr d\theta d\phi$$

$$D = \frac{1}{\pi a^2} \int_{\phi=0}^{\phi=2\pi} \int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} e^{-2\sqrt{r^2+R^2-2rR\cos\theta}/a} r \sin\theta d\theta dr d\phi$$

$$y \equiv \sqrt{r^2+R^2-2rR\cos\theta} \qquad d\left(y^2\right)=2ydy=2rR\sin\theta d\theta$$

$$\frac{y}{R}dy = r\sin\theta d\theta$$

$$D=\frac{1}{\pi a^2}\int_{\phi=0}^{\phi=2\pi}\int_{\theta=0}^{\theta=\pi}\int_{r=0}^{r=\infty} e^{-2y/a}\left(\frac{y}{R}dy\right)drd\phi$$

$$y_1=\sqrt{r^2+R^2-2rR\cos 0}=\sqrt{r^2-2rR+R^2}=\sqrt{\left(r-R\right)^2}=\left|r-R\right|$$

$$y_2=\sqrt{r^2+R^2-2rR\cos\pi}=\sqrt{r^2+2rR+R^2}=\sqrt{\left(r+R\right)^2}=r+R$$

$$D=\frac{1}{\pi Ra^2}2\pi\int_{r=0}^{r=\infty}\int_{y=r-R}^{y=r+R} ye^{-2y/a}dydr$$

$$D=\frac{2}{Ra^2}\int_{r=0}^{r=\infty}\int_{y=|r-R|}^{y=r+R} ye^{-2y/a}dydr$$

$$D=\frac{2}{Ra^2}\int_{r=0}^{r=R}\left[-\frac{a}{4}e^{-2y/a}\left(a+2y\right)\right]_{|r-R|}^{r+R}dr$$

$$D=\frac{2}{Ra^2}\int_{r=0}^{r=\infty}\left[-\frac{a}{4}e^{-2(r+R)/a}\left(a+2\left(r+R\right)\right)\right]-\left[-\frac{a}{4}e^{-2|r-R|/a}\left(a+2\left|r-R\right|\right)\right]dr$$

$$D=\frac{1}{aR}\int -e^{-2(r+R)/a}\left(\frac{a}{2}+r+R\right)dr+\frac{1}{aR}\int e^{-2|r-R|/a}\left(\frac{a}{2}+\left|r-R\right|\right)dr$$

$$\begin{aligned} D \quad = \quad & \frac{1}{aR}\int_0^\infty -e^{-2(r+R)/a}\left(\frac{a}{2}+r+R\right)dr \\ & +\frac{1}{aR}\int_0^R e^{-2(R-r)/a}\left(\frac{a}{2}+R-r\right)dr \\ & +\frac{1}{aR}\int_R^\infty e^{-2(r-R)/a}\left(\frac{a}{2}+r-R\right)dr \end{aligned}$$

$$
\begin{aligned}
D &= \frac{1}{aR}e^{-2R/a}\int_0^\infty -e^{-2r/a}\left(\frac{a}{2}+r+R\right)dr \\
&\quad +\frac{1}{aR}e^{-2R/a}\int_0^R e^{2r/a}\left(\frac{a}{2}+R-r\right)dr \\
&\quad +\frac{1}{aR}e^{2R/a}\int_R^\infty e^{-2r/a}\left(\frac{a}{2}+r-R\right)dr
\end{aligned}
$$

$$
\begin{aligned}
D &= \frac{1}{aR}e^{-2R/a}\left[-\frac{a}{2}\left(a+R\right)\right] \\
&\quad +\frac{1}{aR}e^{-2R/a}\left[\frac{a}{2}\left(a\left(e^{2R/a}-1\right)-R\right)\right] \\
&\quad +\frac{1}{aR}e^{2R/a}\left[\frac{1}{2}a^2e^{-2R/a}\right]
\end{aligned}
$$

$$
\begin{aligned}
D &= e^{-2R/a}\left[-\frac{1}{2R}\left(a+R\right)\right] \\
&\quad +e^{-2R/a}\left[\frac{1}{2R}\left(ae^{2R/a}-a-R\right)\right] \\
&\quad +e^{2R/a}\left[\frac{1}{2R}ae^{-2R/a}\right]
\end{aligned}
$$

$$
\begin{aligned}
D &= e^{-2R/a}\left(-\frac{1}{2R}a-\frac{1}{2}\right) \\
&\quad +e^{-2R/a}\left[\frac{a}{2R}e^{2R/a}-\frac{a}{2R}-\frac{1}{2}\right] \\
&\quad +e^{2R/a}\left[\frac{1}{2R}ae^{-2R/a}\right]
\end{aligned}
$$

$$
\begin{aligned}
D &= -\frac{1}{2R}ae^{-2R/a}-\frac{1}{2}e^{-2R/a} \\
&\quad +\frac{a}{2R}-\frac{a}{2R}e^{-2R/a}-\frac{1}{2}e^{-2R/a} \\
&\quad +\frac{1}{2R}a
\end{aligned}
$$

$$
D = -\frac{1}{2R}ae^{-2R/a}-\frac{1}{2}e^{-2R/a}+\frac{a}{2R}-\frac{a}{2R}e^{-2R/a}-\frac{1}{2}e^{-2R/a}+\frac{1}{2R}a
$$

$$
D = -e^{-2R/a}+\frac{a}{R}-\frac{a}{R}e^{-2R/a}
$$

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

Next, for the X integral,

$$X \equiv a \left\langle \psi_0 \left(r_1\right) \left| \frac{1}{r_1} \right| \psi_0 \left(r_2\right) \right\rangle$$

$$X = \frac{1}{\pi a^2} \int \frac{1}{r_1} e^{-(r_1 + r_2)/a} d^3\boldsymbol{r}$$

$$r_1 = r \qquad r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

$$X = \frac{1}{\pi a^2} \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} \frac{1}{r} e^{-\left(r + \sqrt{r^2+R^2-2rR\cos\theta}\right)/a} r^2 \sin\theta dr d\theta d\phi$$

$$X = \frac{1}{\pi a^2} \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} e^{-\left(r + \sqrt{r^2+R^2-2rR\cos\theta}\right)/a} r \sin\theta dr d\theta d\phi$$

$$X = \frac{2}{a^2} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} e^{-\left(r + \sqrt{r^2+R^2-2rR\cos\theta}\right)/a} r \sin\theta dr d\theta$$

By Mathematica,

$$X = \frac{1}{a} e^{-R/a} \left(a + R\right)$$

$$X = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

7.9

$$\psi = A \left[\psi_0 \left(r_1\right) - \psi_0 \left(r_2\right)\right]$$

From equations 7.38 to 7.42, the difference from the addition version of this trial function is the reversal of the sign of the I overlap integral. In equations 7.44 to 7.46, the expectation value of the Hamiltonian also changes, such that X also reverses sign. In it-s original form,

$$\langle H\rangle = \left[1 + 2\frac{(D+X)}{(1+I)}\right] E_1$$

Applying these changes,

$$\langle H\rangle = \left[1 + 2\frac{(D-X)}{(1-I)}\right] E_1$$

Taking equation 7.49 and adding in the disruption from proton-proton repulsion, and finding in units of $-E_1$,

$$F(x) = \frac{\langle H\rangle + V_{pp}}{E_1} = \frac{1}{-E_1}\left[-\frac{2a}{R} + 1 + 2\frac{(D-X)}{(1-I)}\right] E_1$$

$$F(x) = \frac{2a}{R} - 1 - 2\frac{(D-X)}{(1-I)}$$

$$F(x) = \frac{2a}{R} - 1 - 2\frac{\left(\left(\frac{a}{R} - \left(1+\frac{a}{R}\right)e^{-2R/a}\right) - \left(1+\frac{R}{a}\right)e^{-R/a}\right)}{\left(1 - \left(e^{-R/a}\left[1 + \left(\frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right)\right]\right)\right)}$$

$$x \equiv \frac{R}{a}$$

$$F(x) = \frac{2}{x} - 1 - 2\frac{\frac{1}{x} - \left(1+\frac{1}{x}\right)e^{-2x} - (1+x)e^{-x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

$$F(x) = -1 + \frac{2}{x} - \frac{2}{x}\frac{1 - (x+1)e^{-2x} - \left(x + x^2\right)e^{-x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

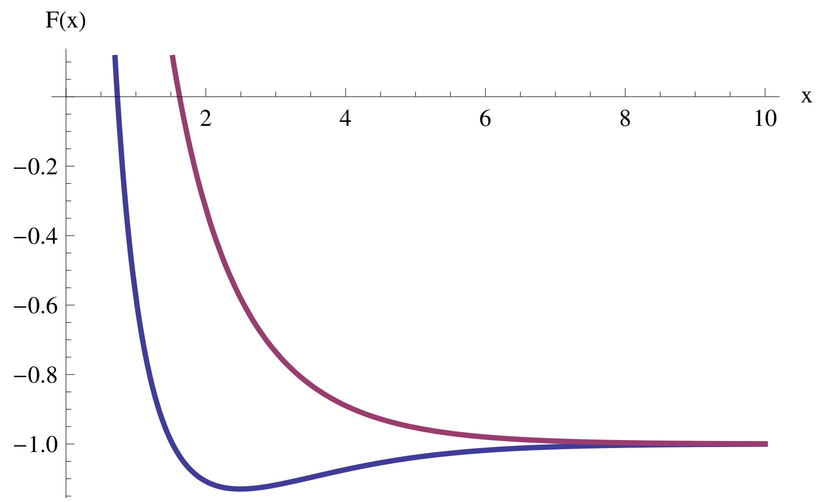
$$F(x) = -1 + \frac{1}{x}\frac{2\left(1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}\right) - 2\left(1 - (x+1)e^{-2x} - \left(x + x^2\right)e^{-x}\right)}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

$$F(x) = -1 + \frac{2}{x}\frac{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x} - 1 + (x+1)e^{-2x} + \left(x + x^2\right)e^{-x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

$$F(x) = -1 + \frac{2}{x}\frac{\left(-1 - x - \frac{1}{3}x^2 + \left(x + x^2\right)\right)e^{-x} + (x+1)e^{-2x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

$$F(x) = -1 + \frac{2}{x}\frac{\left(\frac{2}{3}x^2 - 1\right)e^{-x} + (x+1)e^{-2x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}}$$

Plotting this and the original function,



This one doesn't have the same sort of dip below -1 which would be associated with bonding. Since this is a ratio in terms of $-E_1$, -1 is the point where bonding is no longer lower energy.