The hydrogen molecule ion

Evaluation of integrals

This problem is straightforward and not too hard if you:

1. Use atomic units.
2. Use the substitution $\mu = \cos\theta$.
3. Remember that $\sqrt{x^2} = |x|$, not $\sqrt{x^2} = x$.

First the **overlap integral**

$$I(R) = \langle\alpha|\beta\rangle = \langle\eta_g(r_\alpha)|\eta_g(r_\beta)\rangle \tag{1}$$

where

$$\eta_g(r) = \frac{1}{\sqrt{\pi}}e^{-r} \qquad \text{and} \qquad r_\beta = \sqrt{r_\alpha^2 + R^2 - 2r_\alpha R\cos\theta}.$$

We have

$$\begin{aligned} I(R) &= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^\infty r_\alpha^2\, dr_\alpha\, \frac{1}{\pi}e^{-(r_\alpha + r_\beta)} \\ &= \frac{2\pi}{\pi}\int_0^\infty r_\alpha^2\, dr_\alpha \int_{-1}^{+1} d\mu\, e^{-(r_\alpha + \sqrt{r_\alpha^2 + R^2 - 2r_\alpha R\mu})} \\ &= 2\int_0^\infty r^2\, dr\, e^{-r}\int_{-1}^{+1} d\mu\, e^{-\sqrt{r^2+R^2-2rR\mu}}. \end{aligned}$$

The angular integral is

$$\text{A.I.} = \int_{-1}^{+1} d\mu\, e^{-\sqrt{a-b\mu}} \quad [\text{where } a = r^2 + R^2,\, b = 2rR]. \tag{2}$$

Use the substitution

$$\begin{aligned} x &= -\sqrt{a-b\mu} \\ dx &= -\tfrac{1}{2}\frac{-b}{\sqrt{a-b\mu}}\, d\mu = \frac{1}{2}\frac{b}{-x}\, d\mu \quad \text{whence} \quad d\mu = -\frac{2x}{b}\, dx \end{aligned}$$

to find

$$\begin{aligned} \text{A.I.} &= -\frac{2}{b}\int_{\mu=-1}^{+1} dx\, xe^x \qquad [\![\text{use Dwight 567.1}\ldots]\!] \\ &= -\frac{2}{b}\left[e^x(x-1)\right]_{\mu=-1}^{+1} \\ &= \frac{2}{b}\left[e^{-\sqrt{a-b\mu}}(\sqrt{a-b\mu}+1)\right]_{-1}^{+1} \\ &= \frac{2}{b}\left[e^{-\sqrt{a-b}}(\sqrt{a-b}+1) - e^{-\sqrt{a+b}}(\sqrt{a+b}+1)\right]. \end{aligned}$$

Now

$$\begin{aligned}\sqrt{a-b} &= \sqrt{r^2+R^2-2rR} = \sqrt{(r-R)^2} = |r-R| \\ \sqrt{a+b} &= \sqrt{r^2+R^2+2rR} = \sqrt{(r+R)^2} = r+R\end{aligned}$$

so

$$\text{A.I.} = \frac{1}{rR}\left[e^{-|r-R|}(|r-R|+1) - e^{-(r+R)}(r+R+1)\right]. \tag{3}$$

The overlap integral then is

$$\begin{aligned}I(R) &= \frac{2}{R}\int_0^\infty dr\, re^{-r}\left[e^{-|r-R|}(|r-R|+1) - e^{-(r+R)}(r+R+1)\right] \\ &= \underbrace{\frac{2}{R}\int_0^\infty dr\, re^{-r}\left[e^{-|r-R|}(|r-R|+1)\right]}_{\equiv I_1} \underbrace{-\frac{2}{R}e^{-R}\int_0^\infty dr\, re^{-2r}(r+R+1).}_{\equiv I_2}\end{aligned}$$

The second of these is

$$\begin{aligned}I_2 &= -\frac{2}{R}e^{-R}\left[\int_0^\infty dr\, r^2 e^{-2r} + (R+1)\int_0^\infty dr\, re^{-2r}\right] \qquad [\![\text{use Dwight 567.2 and 567.1 } \ldots]\!] \\ &= -\frac{2}{R}e^{-R}\left[\left[e^{-2r}\left(-\frac{r^2}{2}-\frac{r}{2}-\frac{1}{4}\right)\right]_0^\infty + (R+1)\left[e^{-2r}\left(-\frac{r}{2}-\frac{1}{4}\right)\right]_0^\infty\right] \\ &= -\frac{2}{R}e^{-R}\left[-\left[-\frac{1}{4}\right] + (R+1)\left[\frac{1}{4}\right]\right] \\ &= -e^{-R}\left[\frac{1}{R}+\frac{1}{2}\right].\end{aligned}$$

While the first is

$$\begin{aligned}I_1 &= \frac{2}{R}\int_0^\infty dr\, re^{-r}\left[e^{-|r-R|}(|r-R|+1)\right] \\ &= \frac{2}{R}\left[\int_0^R dr\, re^{-r}\left[e^{r-R}(-r+R+1)\right] + \int_R^\infty dr\, re^{-r}\left[e^{-r+R}(r-R+1)\right]\right] \\ &= \frac{2}{R}\left[e^{-R}\int_0^R dr\,[-r^2+(R+1)r)] + e^R\int_R^\infty dr\, e^{-2r}[r^2-(R-1)r]\right] \\ &= \frac{2}{R}\left[e^{-R}\int_0^R dr\,[-r^2+(R+1)r] + e^R\int_R^\infty dr\, r^2e^{-2r} - e^R(R-1)\int_R^\infty dr\, re^{-2r}\right] \\ &= \frac{2}{R}\left[e^{-R}\left[-\frac{r^3}{3}+(R+1)\frac{r^2}{2}\right]_0^R + e^R\left[e^{-2r}\left(-\frac{r^2}{2}-\frac{r}{2}-\frac{1}{4}\right)\right]_R^\infty - e^R(R-1)\left[e^{-2r}\left(-\frac{r}{2}-\frac{1}{4}\right)\right]_R^\infty\right] \\ &= \frac{2}{R}\left[e^{-R}\left[-\frac{R^3}{3}+(R+1)\frac{R^2}{2}\right] - e^R\left[e^{-2R}\left(-\frac{R^2}{2}-\frac{R}{2}-\frac{1}{4}\right)\right] + e^R(R-1)\left[e^{-2R}\left(-\frac{R}{2}-\frac{1}{4}\right)\right]\right] \\ &= \frac{2}{R}e^{-R}\left[-\tfrac{1}{3}R^3+\tfrac{1}{2}R^3+\tfrac{1}{2}R^2+\tfrac{1}{2}R^2+\tfrac{1}{2}R+\tfrac{1}{4}-\tfrac{1}{2}R^2-\tfrac{1}{4}R+\tfrac{1}{2}R+\tfrac{1}{4}\right] \\ &= e^{-R}\left[\frac{R^2}{3}+R+\frac{3}{2}+\frac{1}{R}\right].\end{aligned}$$

Then

$$I(R) = I_1 + I_2 = e^{-R}\left[\tfrac{1}{3}R^2 + R + 1\right]$$

or, in conventional units

$$I(R) = e^{-R/a_0}\left[\frac{1}{3}\left(\frac{R}{a_0}\right)^2 + \frac{R}{a_0} + 1\right]. \tag{4}$$

Go on to the **direct integral**

$$D(R) = \left\langle \eta_g(r_\alpha) \left| \frac{1}{r_\beta} \right| \eta_g(r_\alpha) \right\rangle \tag{5}$$

Thus

$$\begin{aligned} D(R) &= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} r_\alpha^2\, dr_\alpha\, \frac{1}{\pi} e^{-2r_\alpha} \frac{1}{\sqrt{r_\alpha^2 + R^2 - 2r_\alpha R\cos\theta}} \\ &= \frac{2\pi}{\pi}\int_0^{\infty} r^2\, dr \int_{-1}^{+1} d\mu\, e^{-2r} \frac{1}{\sqrt{r^2 + R^2 - 2rR\mu}}. \end{aligned}$$

Now, what is

$$\int_{-1}^{+1} d\mu\, \frac{1}{\sqrt{a - b\mu}}? \qquad \text{[Where } a = r^2 + R^2,\ b = 2rR.\text{]}$$

It is

$$\begin{aligned} \int_{-1}^{+1} d\mu\, \frac{1}{\sqrt{a-b\mu}} &= \left[-\frac{2}{b}\sqrt{a-b\mu}\right]_{-1}^{+1} = -\frac{2}{b}\left[\sqrt{a-b} - \sqrt{a+b}\right] = \frac{2}{b}\left[\sqrt{a+b} - \sqrt{a-b}\right] \\ &= \frac{1}{rR}\left[\sqrt{r^2 + R^2 + 2rR} - \sqrt{r^2 + R^2 - 2rR}\right] \\ &= \frac{1}{rR}\left[\sqrt{(r+R)^2} - \sqrt{(r-R)^2}\right] \qquad [\![\text{Dangerous curve ahead!}]\!] \\ &= \frac{1}{rR}\left[(r+R) - |r-R|\right] \\ &= \frac{1}{rR}\begin{cases} (r+R) - (R-r) & \text{for } r < R \\ (r+R) - (r-R) & \text{for } r > R \end{cases} \\ &= \frac{1}{rR}\begin{cases} 2r & \text{for } r < R \\ 2R & \text{for } r > R \end{cases} \\ &= \frac{2}{rR}\min\{r, R\}. \end{aligned}$$

Thus

$$\begin{aligned} D(R) &= \frac{4}{R}\int_0^{\infty} r^2\, dr\, \frac{1}{r}\min\{r,R\} e^{-2r} \\ &= \frac{4}{R}\int_0^{\infty} dr\, r\min\{r,R\} e^{-2r} \\ &= \frac{4}{R}\int_0^{R} dr\, r^2 e^{-2r} + \frac{4}{R}\int_R^{\infty} dr\, rRe^{-2r} \\ &= \frac{4}{R}\int_0^{R} dr\, r^2 e^{-2r} + 4\int_R^{\infty} dr\, re^{-2r} \qquad [\![\text{use Dwight 567.2 and 567.1}\ldots]\!] \end{aligned}$$

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

In conventional units,

$$
D(R) = \frac{a_0}{R}-\left(1+\frac{a_0}{R}\right)e^{-2R/a_0}. \tag{6}
$$

Onward and upward! Last we work the **exchange integral**

$$
\begin{aligned}
X(R) &= \left\langle \eta_g(r_\alpha)\left|\frac{1}{r_\alpha}\right|\eta_g(r_\beta)\right\rangle \qquad \text{with } \eta_g(r)=\frac{1}{\sqrt{\pi}}e^{-r} \\
&= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^\infty r_\alpha^2\, dr_\alpha\, \frac{1}{\pi}e^{-(r_\alpha+r_\beta)}\frac{1}{r_\alpha}
\end{aligned} \tag{7}
$$

but $r_\alpha + r_\beta = r_\alpha + \sqrt{r_\alpha^2+R^2-2r_\alpha R\cos\theta}$, so

$$
\begin{aligned}
X(R) &= \frac{2\pi}{\pi}\int_0^\infty r_\alpha\, dr_\alpha \int_{-1}^{+1} d\mu\, e^{-(r_\alpha+\sqrt{r_\alpha^2+R^2-2r_\alpha R\mu})} \\
&= 2\int_0^\infty r\, dr\, e^{-r}\int_{-1}^{+1} d\mu\, e^{-\sqrt{r^2+R^2-2rR\mu}}
\end{aligned}
$$

The angular integral is the same one defined in equation (2) and evaluated in equation (3). It follows that

$$
\begin{aligned}
X(R) &= \frac{2}{R}\int_0^\infty dr\, e^{-r}\left[e^{-|r-R|}(|r-R|+1)-e^{-(r+R)}(r+R+1)\right] \\
&= \underbrace{\frac{2}{R}\int_0^\infty dr\, e^{-r}\left[e^{-|r-R|}(|r-R|+1)\right]}_{\equiv X_1}\underbrace{-\frac{2}{R}e^{-R}\int_0^\infty dr\, e^{-2r}(r+R+1).}_{\equiv X_2}
\end{aligned}
$$

The second of these is

$$
\begin{aligned}
X_2 &= -\frac{2}{R}e^{-R}\left[\int_0^\infty dr\, re^{-2r}+(R+1)\int_0^\infty dr\, e^{-2r}\right] \qquad [\![\text{use Dwight 565.1 and 567.1}\ldots]\!] \\
&= -\frac{2}{R}e^{-R}\left[\left[e^{-2r}\left(-\frac{r}{2}-\frac{1}{4}\right)\right]_0^\infty+(R+1)\left[e^{-2r}\left(-\frac{1}{2}\right)\right]_0^\infty\right] \\
&= -\frac{2}{R}e^{-R}\left[-\left[-\frac{1}{4}\right]+(R+1)\left[\frac{1}{2}\right]\right] \\
&= -e^{-R}\left[\frac{3}{2R}+1\right].
\end{aligned}
$$

While the first is

$$
\begin{aligned}
X_1 &= \frac{2}{R}\int_0^\infty dr\, e^{-r}\left[e^{-|r-R|}(|r-R|+1)\right] \\
&= \frac{2}{R}\left[\int_0^R dr\, e^{-r}\left[e^{r-R}(-r+R+1)\right] + \int_R^\infty dr\, e^{-r}\left[e^{-r+R}(r-R+1)\right]\right] \\
&= \frac{2}{R}\left[e^{-R}\int_0^R dr\,(-r+R+1) + e^R\int_R^\infty dr\, e^{-2r}(r-R+1)\right] \\
&= \frac{2}{R}\left[e^{-R}\int_0^R dr\,(-r+R+1) + e^R\int_R^\infty dr\, re^{-2r} + e^R(1-R)\int_R^\infty dr\, e^{-2r}\right] \\
&= \frac{2}{R}\left[e^{-R}\left[-\frac{r^2}{2}+(R+1)r\right]_0^R + e^R\left[e^{-2r}\left(-\frac{r}{2}-\frac{1}{4}\right)\right]_R^\infty + e^R(1-R)\left[e^{-2r}\left(-\frac{1}{2}\right)\right]_R^\infty\right] \\
&= \frac{2}{R}\left[e^{-R}\left[-\frac{R^2}{2}+(R+1)R\right] - e^R\left[e^{-2R}\left(-\frac{R}{2}-\frac{1}{4}\right)\right] - e^R(1-R)\left[e^{-2R}\left(-\frac{1}{2}\right)\right]\right] \\
&= \frac{2}{R}e^{-R}\left[\tfrac{1}{2}R^2 + R + \tfrac{1}{2}R + \tfrac{1}{4} - \tfrac{1}{2}R + \tfrac{1}{2}\right] \\
&= e^{-R}\left[R + 2 + \frac{3}{2R}\right].
\end{aligned}
$$

Then

$$X(R) = X_1 + X_2 = e^{-R}\left[R + 2 + \frac{3}{2R} - \frac{3}{2R} - 1\right] = e^{-R}\left[R+1\right].$$

In conventional units,

$$X(R) = e^{-R/a_0}\left[1 + \frac{R}{a_0}\right].$$

I have plotted the integrals $I(R)$, $D(R)$, and $X(R)$ as functions of R using an excel spreadsheet. But I haven't been able to insert the plot into this document because excel (like most Micro$oft products) seems to be brain dead. You may download the spreadsheet as `HydrogenMoleculeIon.xls`.

Thinking about integrals

The nuclear potential energy is easy: it's

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{R} \quad \text{or, in atomic units,} \quad \frac{1}{R}$$

The electronic potential and kinetic energies are a bit harder. We will use atomic units throughout. The trial wavefunction is

$$\psi_+(\mathbf{r}) = C_+[\eta_\alpha(\mathbf{r}) + \eta_\beta(\mathbf{r})] = C_+(|\alpha\rangle + |\beta\rangle)$$

where $\eta(\mathbf{r}) = e^{-r}/\sqrt{\pi}$.

The mean kinetic energy is

$$\begin{aligned}
\langle\widehat{KE}\rangle &= C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{KE})(|\alpha\rangle + |\beta\rangle)\right] \\
&= C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{KE})|\alpha\rangle\right] + C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{KE})|\beta\rangle\right] \\
&= 2C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{KE})|\alpha\rangle\right] \\
&= 2C_+^2\left[\langle\alpha|\widehat{KE}|\alpha\rangle + \langle\beta|\widehat{KE}|\alpha\rangle\right]
\end{aligned}$$

The value of $\langle\alpha|\widehat{KE}|\alpha\rangle$ comes from direct calculation, or from the virial theorem ($\langle\widehat{KE}\rangle = -\frac{1}{2}\langle\widehat{PE}\rangle$ for the hydrogen atom), or from looking it up in a book. The answer is $\langle\widehat{KE}\rangle = +\frac{1}{2}$ (in conventional units, $\langle\widehat{KE}\rangle = +\text{Ry}$).

Meanwhile

$$\begin{aligned}
\widehat{KE}\,\eta(r) &= -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\eta(r)}{\partial r}\right)\right] \\
&= -\frac{1}{2}\eta(r) + \frac{1}{r}\eta(r)
\end{aligned}$$

so

$$\begin{aligned}
\langle\beta|\widehat{KE}|\alpha\rangle &= -\frac{1}{2}\langle\beta|\alpha\rangle + \left\langle\beta\left|\frac{1}{r_\alpha}\right|\alpha\right\rangle \\
&= -\tfrac{1}{2}I(R) + X(R).
\end{aligned}$$

Recalling that $C_+^2 = 1/[2(1+I(R))]$ gives

$$\langle\widehat{KE}\rangle = \frac{1}{2}\frac{1 - I(R) + 2X(R)}{1 + I(R)}.$$

We could find the potential energy either directly or else (given that we know $\langle\hat{H}\rangle$) through $\langle\hat{H}\rangle = \langle\widehat{KE}\rangle + \langle\widehat{PE}\rangle$. The direct approach is

$$\begin{aligned}
\langle\widehat{PE}\rangle &= C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{PE})(|\alpha\rangle + |\beta\rangle)\right] \\
&= C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{PE})|\alpha\rangle\right] + C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{PE})|\beta\rangle\right] \\
&= 2C_+^2\left[(\langle\alpha| + \langle\beta|)(\widehat{PE})|\alpha\rangle\right] \\
&= 2C_+^2\left[\langle\alpha|\widehat{PE}|\alpha\rangle + \langle\beta|\widehat{PE}|\alpha\rangle\right] \\
&= -2C_+^2\left[\left\langle\alpha\left|\frac{1}{r_\alpha} + \frac{1}{r_\beta}\right|\alpha\right\rangle + \left\langle\beta\left|\frac{1}{r_\alpha} + \frac{1}{r_\beta}\right|\alpha\right\rangle\right] \\
&= -2C_+^2\left[\left\langle\alpha\left|\frac{1}{r_\alpha}\right|\alpha\right\rangle + D(R) + 2X(R)\right]
\end{aligned}$$

The value of $\langle\alpha|\widehat{PE}|\alpha\rangle$ comes from direct calculation, or from the virial theorem, or from looking it up in a book. The answer is $\langle\widehat{PE}\rangle = -1$ (in conventional units, $\langle\widehat{PE}\rangle = -2\text{Ry}$).

Recalling that $C_+^2 = 1/[2(1+I(R))]$ gives

$$\langle \widehat{PE} \rangle = -\frac{1+D(R)+2X(R)}{1+I(R)}.$$

The values of these energies are calculated and plotted in the excel spreadsheet

`HydrogenMoleculeIon.xls`.

The plot shows energies in atomic units... remember that an energy of $\frac{1}{2}$ in atomic units corresponds to one Ry.