Report FYS4411 - Project 1

Filip Sund
filipsu@fys.uio.no

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$$
\begin{aligned}
E_{L2} &= \frac{1}{\Psi_T}\hat{\mathbf{H}}\Psi_T \\
&= \frac{1}{\Psi_T}\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\exp\left(-\alpha(r_1+r_2) + \frac{r_{12}}{2(1+\beta r_{12})}\right)
\end{aligned}
$$

We first do the derivative of the first half of the core of exponential

$$
\begin{aligned}
\frac{\nabla_1^2}{2}\Big(-\alpha(r_1+r_2)\Big) &= \frac{1}{2}\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left[r_1^2\frac{\partial}{\partial r_1}\Big(-\alpha(r_1+r_2)\Big)\right] \\
&= \frac{1}{2r_1^2}\frac{\partial}{\partial r_1}\left[r_1^2 - \alpha\right] \\
&= \frac{1}{2r_1^2}\Big(-2r_1\alpha\Big) \\
&= -\frac{\alpha}{r_1}
\end{aligned}
$$

using the radial part of the Laplacian in spherical coordinates. We then do the derivative of the second part of the exponential with regards to r_1

$$
\frac{\nabla_1^2}{2}\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) = \frac{1}{2}\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left[r_1^2\frac{\partial}{\partial r_1}\left(\frac{r_{12}}{2(1+\beta r_{12})}\right)\right]. \tag{1}
$$

Now we focus on just the first derivative in the equation above

$$
\begin{aligned}
\frac{\partial}{\partial r_1}\left(\frac{r_{12}}{2(1+\beta r_{12})}\right) &= \frac{\left(\frac{\partial}{\partial r_1}r_{12}\right)\cdot 2(1+\beta r_{12}) - r_{12}\cdot 2\beta\left(\frac{\partial}{\partial r_1}r_{12}\right)}{4(1+\beta r_{12})^2} \\
&= \frac{\left(\frac{\partial}{\partial r_1}r_{12}\right)}{2(1+\beta r_{12})^2},
\end{aligned}
$$

where $\frac{\partial}{\partial r_1}r_{12}$ is yet do be decided. We can then continue with the second derivative in (1)

$$
\frac{\partial}{\partial r_1}\left[r_1^2\frac{\partial}{\partial r_1}\left(\frac{r_{12}}{2(1+\beta r_{12})}\right)\right] = \frac{\partial}{\partial r_1}\left[\frac{r_1^2\left(\frac{\partial}{\partial r_1}r_{12}\right)}{2(1+\beta r_{12})^2}\right]. \tag{2}
$$

Now we see that we need the derivatives of the numerator and denominator, which we find separately as

$$\frac{\partial}{\partial r_1}\left[r_1^2\left(\frac{\partial}{\partial r_1}r_{12}\right)\right] = 2r_1\left(\frac{\partial}{\partial r_1}r_{12}\right) + r_1^2\left(\frac{\partial^2}{\partial r_1^2}r_{12}\right),$$

and

$$\begin{aligned}\frac{\partial}{\partial r_1}2(1+\beta r_{12})^2 &= 4\beta\frac{\partial}{\partial r_1}r_{12} + 2\beta^2\frac{\partial}{\partial r_1}r_{12}^2\\ &= 4\beta\frac{\partial}{\partial r_1}r_{12} + 4\beta^2 r_{12}\frac{\partial}{\partial r_1}r_{12}\\ &= 4\beta\left(\frac{\partial}{\partial r_1}r_{12}\right)(1+\beta r_{12}).\end{aligned}$$

Now we can put this all toghether to to solve (2), yelding

$$\begin{aligned}&\frac{\left[2r_1\left(\frac{\partial}{\partial r_1}r_{12}\right) + r_1^2\left(\frac{\partial^2}{\partial r_1^2}r_{12}\right)\right]\cdot 2(1+\beta r_{12})^2 - r_1^2\left(\frac{\partial}{\partial r_1}r_{12}\right)\cdot 4\beta\left(\frac{\partial}{\partial r_1}r_{12}\right)(1+\beta r_{12})}{4(1+\beta r_{12})^4}\\ &= \frac{\left[r_1\left(\frac{\partial}{\partial r_1}r_{12}\right) + \frac{r_1^2}{2}\left(\frac{\partial^2}{\partial r_1^2}r_{12}\right)\right](1+\beta r_{12}) - r_1^2\left(\frac{\partial}{\partial r_1}r_{12}\right)\beta\left(\frac{\partial}{\partial r_1}r_{12}\right)}{(1+\beta r_{12})^3}\end{aligned}$$

r-derivatives

$$\begin{aligned}\frac{\partial}{\partial r_1}r_{12} &= \frac{\partial}{\partial r_1}\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}\\ &= \frac{\partial}{\partial r_1}\sqrt{(r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2}\\ &= \left(\frac{1}{2r_{12}}\right)\frac{\partial}{\partial r_1}\left[(r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2\right]\\ &= \frac{1}{2r_{12}}\left[2(x_1-x_2)(\sin\theta_1\cos\phi_1)+2(y_1-y_2)(\sin\theta_1\sin\phi_1)+2(z_1-z_2)(\cos\theta_1)\right]\\ &= \frac{1}{r_{12}}\left[(x_1-x_2)\frac{x_1}{r_1}+(y_1-y_2)\frac{y_1}{r_1}+(z_1-z_2)\frac{z_1}{r_1}\right]\\ &= \frac{1}{r_1r_{12}}\left[r_1^2-x_1x_2-y_1y_2-z_1z_2\right]\\ &= \frac{1}{r_1r_{12}}\left[r_1^2-\mathbf{r}_1\mathbf{r}_2\right]\end{aligned}$$

$$\frac{\partial^2}{\partial r_1^2}r_{12} = \frac{\partial}{\partial r_1}\left[\frac{1}{r_{12}}\left(r_1-x_2\frac{x_1}{r_1}-y_2\frac{y_1}{r_1}-z_2\frac{z_1}{r_1}\right)\right]$$

$$
\begin{aligned}
\frac{\partial}{\partial r_1}\frac{1}{r_{12}} &= \frac{\partial}{\partial r_1}\Big((x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2\Big)^{-1/2} \\
&= \left(-\frac{1}{2r_{12}}\right)\frac{\partial}{\partial r_1}\Big((x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2\Big) \\
&= -\frac{1}{2r_{12}}\frac{\partial}{\partial r_1}\Big((r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2\Big)
\end{aligned}
$$

θ-derivatives

$$
\begin{aligned}
\frac{\partial}{\partial\theta_1}r_{12} &= \frac{\partial}{\partial\theta_1}\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2} \\
&= \left(\frac{1}{2r_{12}}\right)\frac{\partial}{\partial\theta_1}\Big[(r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2\Big] \\
&= \frac{1}{2r_{12}}\Big[2(x_1-x_2)r_1\cos\theta_1\cos\phi_1+2(y_1-y_2)r_1\cos\theta_1\sin\phi_1-2(z_1-z_2)r_1\sin\theta_1\Big] \\
&= \frac{r_1}{r_{12}}\Big[(x_1-x_2)\cos\theta_1\cos\phi_1+(y_1-y_2)\cos\theta_1\sin\phi_1-(z_1-z_2)\sin\theta_1\Big]
\end{aligned}
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\begin{aligned}
\frac{\partial}{\partial\theta_1}\left(\sin\theta_1\frac{\partial}{\partial\theta_1}r_{12}\right) &= \frac{\partial}{\partial\theta_1}\left(\sin\theta_1\frac{r_1}{r_{12}}\Big[(x_1-x_2)\cos\theta_1\cos\phi_1+(y_1-y_2)\cos\theta_1\sin\phi_1-(z_1-z_2)\sin\theta_1\Big]\right) \\
&= \frac{\partial}{\partial\theta_1}\left[\frac{1}{r_{12}}\Big((x_1-x_2)x_1\cos\theta_1+(y_1-y_2)y_1\cos\theta_1-(z_1-z_2)r_1\sin^2\theta_1\Big)\right]
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial}{\partial\theta_1}\frac{1}{r_{12}} &= \frac{\partial}{\partial\theta_1}\Big[(r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2\Big]^{-1/2} \\
&= \left(-\frac{1}{2r_{12}^3}\right)\frac{\partial}{\partial\theta_1}\Big[(r_1\sin\theta_1\cos\phi_1-x_2)^2+(r_1\sin\theta_1\sin\phi_1-y_2)^2+(r_1\cos\theta_1-z_2)^2\Big] \\
&= -\frac{1}{2r_{12}^3}\Big[2(x_1-x_2)r_1\cos\theta_1\cos\phi_1+2(y_1-y_2)r_1\cos\theta_1\sin\phi_1-2(z_1-z_2)r_1\sin\theta_1\Big] \\
&= -\frac{r_1}{r_{12}^3}\Big[(x_1-x_2)\cos\theta_1\cos\phi_1+(y_1-y_2)\cos\theta_1\sin\phi_1-(z_1-z_2)\sin\theta_1\Big]
\end{aligned}
$$

$$
\frac{\partial}{\partial\theta_1}\Big((x_1-x_2)x_1\cos\theta_1+(y_1-y_2)y_1\cos\theta_1-(z_1-z_2)r_1\sin^2\theta_1\Big)
$$

$$
\begin{aligned}
\frac{\partial}{\partial\theta_1}(x_1-x_2)x_1\cos\theta_1 &= \frac{\partial}{\partial\theta_1}\Big(x_1^2\cos\theta_1-x_1x_2\cos\theta_1\Big) \\
&= r_1^2\cos^2\phi_1\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta_1\cos\theta_1-x_2r_1\cos\phi_1\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin\theta_1\cos\theta_1
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial}{\partial \theta_1}(y_1 - y_2)y_1 \cos\theta_1 &= \frac{\partial}{\partial \theta_1}\Big(y_1^2 \cos\theta_1 - y_1 y_2 \cos\theta_1\Big) \\
&= r_1^2 \sin^2\phi_1 \frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta_1\cos\theta_1 - y_2 r_1 \sin\phi_1 \frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin\theta_1\cos\theta_1
\end{aligned}
$$

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\begin{aligned}
&\frac{\partial}{\partial \theta_1}(x_1 - x_2)x_1 \cos\theta_1 + \frac{\partial}{\partial \theta_1}(y_1 - y_2)y_1 \cos\theta_1 \\
&= r_1^2(\sin^2\phi_1 + \cos^2\phi_1)\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta_1\cos\theta_1 - r_1(x_2\cos\phi_1 + y_2\sin\phi_1)\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin\theta_1\cos\theta_1 \\
&= r_1^2\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta_1\cos\theta_1 - r_1(x_2\cos\phi_1 + y_2\sin\phi_1)\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin\theta_1\cos\theta_1
\end{aligned}
$$

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\begin{aligned}
\frac{\partial}{\partial \theta_1}(z_1 - z_2)r_1 \sin^2\theta_1 &= \frac{\mathrm{d}}{\mathrm{d}\theta_1} r_1\cos\theta_1 r_1 \sin^2\theta_1 - \frac{\mathrm{d}}{\mathrm{d}\theta_1} z_2 r_1 \sin^2\theta_1 \\
&= r_1^2\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta_1\cos\theta_1 - r_1 z_2 \frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta
\end{aligned}
$$

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\begin{aligned}
&\frac{\partial}{\partial \theta_1}(x_1 - x_2)x_1 \cos\theta_1 + \frac{\partial}{\partial \theta_1}(y_1 - y_2)y_1 \cos\theta_1 - \frac{\partial}{\partial \theta_1}(z_1 - z_2)r_1 \sin^2\theta_1 \\
&= -r_1(x_2\cos\phi_1 + y_2\sin\phi_1)\frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin\theta_1\cos\theta_1 - r_1 z_2 \frac{\mathrm{d}}{\mathrm{d}\theta_1}\sin^2\theta \\
&= -r_1(x_2\cos\phi_1 + y_2\sin\phi_1)(\cos^2\theta_1 - \sin^2\theta_1) - z_2 r_1 2\sin\theta_1\cos\theta_1
\end{aligned}
$$

ϕ-derivatives

$$
\begin{aligned}
\frac{\partial}{\partial \phi_1} r_{12} &= \frac{\partial}{\partial \phi_1}\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \\
&= \frac{\partial}{\partial \phi_1}\sqrt{(r_1\sin\theta_1\cos\phi_1 - x_2)^2 + (r_1\sin\theta_1\sin\phi_1 - y_2)^2 + (r_1\cos\theta_1 - z_2)^2} \\
&= \left(\frac{1}{2r_{12}}\right)\frac{\partial}{\partial \phi_1}\Big[(r_1\sin\theta_1\cos\phi_1 - x_2)^2 + (r_1\sin\theta_1\sin\phi_1 - y_2)^2 + (r_1\cos\theta_1 - z_2)^2\Big] \\
&= \frac{1}{2r_{12}}\Big[-2(x_1 - x_2)r_1\sin\theta_1\sin\phi_1 + 2(y_1 - y_2)r_1\sin\theta_1\cos\phi_1\Big] \\
&= \frac{1}{r_{12}}\Big[-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big]
\end{aligned}
$$

$$
\frac{\partial^2}{\partial \phi_1^2} r_{12} = \frac{\partial}{\partial \phi_1}\left[\frac{1}{r_{12}}\Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big)\right]
$$

$$
\begin{aligned}
\frac{\partial}{\partial \phi_1}(x_1 - x_2)y_1 &= \frac{\partial}{\partial \phi_1}\Big(x_1 y_1 - x_2 y_1\Big) \\
&= \frac{\partial}{\partial \phi_1}\Big(r_1^2 \sin\theta_1^2 \sin\phi_1 \cos\phi_1 - x_2 r_1 \sin\theta_1 \sin\phi_1\Big) \\
&= r_1^2 \sin\theta_1 \frac{\mathrm{d}}{\mathrm{d}\phi_1} \sin\phi_1 \cos\phi_1 - x_2 r_1 \sin\theta_1 \cos\phi_1 \\
&= r_1^2 \sin\theta_1 \frac{\mathrm{d}}{\mathrm{d}\phi_1} \sin\phi_1 \cos\phi_1 - x_1 x_2
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial}{\partial \phi_1}(y_1 - y_2)x_1 &= \frac{\partial}{\partial \phi_1}\Big(y_1 x_1 - y_2 x_1\Big) \\
&= \frac{\partial}{\partial \phi_1}\Big(r_1^2 \sin^2\theta_1 \sin\phi_1 \cos\phi_1 - y_2 r_1 \sin\theta_1 \cos\phi_1\Big) \\
&= r_1^2 \sin^2\theta_1 \frac{\mathrm{d}}{\mathrm{d}\phi_1} \sin\phi_1 \cos\phi_1 + y_2 r_1 \sin\theta_1 \sin\phi_1 \\
&= r_1^2 \sin^2\theta_1 \frac{\mathrm{d}}{\mathrm{d}\phi_1} \sin\phi_1 \cos\phi_1 + y_1 y_2
\end{aligned}
$$

$$
\frac{\partial}{\partial \phi_1}\Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big) = x_1 x_2 + y_1 y_2
$$

$$
\begin{aligned}
\frac{\partial}{\partial \phi_1}\frac{1}{r_{12}} &= \frac{\partial}{\partial \phi_1}\Big[(r_1 \sin\theta_1 \cos\phi_1 - x_2)^2 + (r_1 \sin\theta_1 \sin\phi_1 - y_2)^2 + (r_1 \cos\theta_1 - z_2)^2\Big]^{-1/2} \\
&= \left(-\frac{1}{2r_{12}^3}\right)\frac{\partial}{\partial \phi_1}\Big[(r_1 \sin\theta_1 \cos\phi_1 - x_2)^2 + (r_1 \sin\theta_1 \sin\phi_1 - y_2)^2 + (r_1 \cos\theta_1 - z_2)^2\Big] \\
&= -\frac{1}{2r_{12}^3}\Big[-2(x_1 - x_2) r_1 \sin\theta_1 \sin\phi_1 + 2(y_1 - y_2) r_1 \sin\theta_1 \cos\phi_1\Big] \\
&= -\frac{1}{r_{12}^3}\Big[-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big]
\end{aligned}
$$

$$
\begin{aligned}
&\left(\frac{\partial}{\partial \phi_1}\frac{1}{r_{12}}\right) \cdot \Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big) \\
&= -\frac{1}{r_{12}^3}\Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big) \cdot \Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big) \\
&= -\frac{1}{r_{12}^3}\Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big)^2
\end{aligned}
$$

$$
\begin{aligned}
&\frac{1}{r_{12}} \cdot \frac{\partial}{\partial \phi_1}\Big(-(x_1 - x_2)y_1 + (y_1 - y_2)x_1\Big) \\
&= \frac{1}{r_{12}} \cdot \Big(x_1 x_2 + y_1 y_2\Big)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial^2}{\partial \phi_1^2} r_{12} &= \frac{1}{r_{12}}\Big(x_1 x_2 + y_1 y_2\Big) - \frac{1}{r_{12}^3}\Big((y_1 - y_2)x_1 - (x_1 - x_2)y_1\Big)^2 \\
&= \frac{1}{r_{12}}\Big(x_1 x_2 + y_1 y_2\Big) - \frac{1}{r_{12}^3}\Big(x_2 y_1 - x_1 y_2\Big)^2
\end{aligned}
$$

NEW STUFF

$$
\frac{\partial}{\partial x_1} r_{12} = \frac{1}{r_{12}}(x_1 - x_2)
$$

$$
\begin{aligned}
\frac{\partial^2}{\partial x_1^2} r_{12} &= \frac{\partial}{\partial x_1}\frac{1}{r_{12}}(x_1 - x_2) \\
&= \frac{1}{r_{12}} - \frac{(x_1 - x_2)^2}{r_{12}^3}
\end{aligned}
$$

$$
\frac{\partial}{\partial x_1}\frac{1}{r_{12}} = -\frac{x_1 - x_2}{r_{12}^3}
$$