CSE 389D: Mathematical Modeling **Spring 2025**

Problem Set 4

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Problem 4.1

Part a

Recall that the spin operator is given by $\hat{S} = \frac{1}{2}\hbar\sigma$ where $\sigma = \mathbb{o}_x u_x + \mathbb{o}_y u_y + \mathbb{o}_z u_z$. Then we have that the expectation of the spin operator is

$$\langle\Psi|\,\hat{S}\,|\Psi\rangle = \frac{\hbar}{2}\left[\langle\Psi|\,\mathbb{o}_x\,|\Psi\rangle\,u_x + \langle\Psi|\,\mathbb{o}_y\,|\Psi\rangle\,u_y + \langle\Psi|\,\mathbb{o}_z\,|\Psi\rangle\,u_z\right]$$

and we have that

$$\begin{aligned}\langle\Psi|\,\mathbb{o}_x\,|\Psi\rangle = \begin{bmatrix}u^*(r) & d^*(r)\end{bmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{bmatrix}u(r)\\ d(r)\end{bmatrix} &= u^*(r)d(r) + d^*(r)u(r)\\ &= \operatorname{Re}(u^*d) + i\operatorname{Im}(u^*d) + \operatorname{Re}(u^*d) - i\operatorname{Im}(u^*d)\\ &= 2\operatorname{Re}(u^*d)\end{aligned}$$

and

$$\begin{aligned}\langle\Psi|\,\mathbb{o}_y\,|\Psi\rangle = \begin{bmatrix}u^*(r) & d^*(r)\end{bmatrix}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{bmatrix}u(r)\\ d(r)\end{bmatrix} &= -iu^*(r)d(r) + id^*(r)u(r)\\ &= -i\operatorname{Re}(u^*d) + \operatorname{Im}(u^*d) + i\operatorname{Re}(u^*d) + \operatorname{Im}(u^*d)\\ &= 2\operatorname{Im}(u^*d)\end{aligned}$$

lastly,

$$\begin{aligned}\langle\Psi|\,\mathbb{o}_z\,|\Psi\rangle = \begin{bmatrix}u^*(r) & d^*(r)\end{bmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{bmatrix}u(r)\\ d(r)\end{bmatrix} &= u^*(r)u(r) - d^*(r)d(r)\\ &= |u|^2 - |d|^2\end{aligned}$$

and hence then expectation value of the spin operator on this spinsor is given by

$$\langle\Psi|\,\hat{S}\,|\Psi\rangle = \frac{\hbar}{2}\left[2\operatorname{Re}(u^*d)u_x + 2\operatorname{Im}(u^*d)u_y + (|u|^2 - |d|^2)u_z\right]$$

Part b

We compute the norm of $\langle\Psi|\,\hat{S}\,|\Psi\rangle$ as

$$
\begin{aligned}
|\langle\Psi|\,\hat{S}\,|\Psi\rangle| &= \frac{\hbar}{2}\sqrt{4\operatorname{Re}(u^*d)^2 + 4\operatorname{Im}(u^*d)^2 + |u|^4 - 2|u|^2|d|^2 + |d|^4} \\
&= \frac{\hbar}{2}\sqrt{4|u^*d|^2 + |u|^4 - 2|u|^2|d|^2 + |d|^4} \\
&= \frac{\hbar}{2}\sqrt{4|u|^2|d|^2 + |u|^4 - 2|u|^2|d|^2 + |d|^4} \\
&= \frac{\hbar}{2}\sqrt{|u|^4 + 2|u|^2|d|^2 + |d|^4} \\
&= \frac{\hbar}{2}\sqrt{(|u|^2 + |d|^2)^2} \\
&= \frac{\hbar}{2}\sqrt{|\Psi|^2} = \frac{\hbar}{2}
\end{aligned}
$$

Part c

Consider

$$
\exp\left(i\varphi\frac{\hat{S}_z}{\hbar}\right) = \sum_{n=0}^{\infty}\frac{\left(i\varphi\frac{\hat{S}_z}{\hbar}\right)^n}{n!} = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i\varphi}{2}\right)^n\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}^n
$$

note that for n even we have that

$$
\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}^n = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}
$$

and remains unchanged for n odd, thus we can write the above as

$$
\exp\left(i\varphi\frac{\hat{S}_z}{\hbar}\right) = \begin{pmatrix}\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i\varphi}{2}\right)^n & 0\\ 0 & \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i\varphi}{2}\right)^n\end{pmatrix} = \begin{pmatrix}\exp\left(\frac{i\varphi}{2}\right) & 0\\ 0 & \exp\left(-\frac{i\varphi}{2}\right)\end{pmatrix}
$$

Part d

Note that

$$
\Psi' = \exp\left(i\varphi\frac{\hat{S}_z}{\hbar}\right)\Psi = \begin{pmatrix}\exp\left(\frac{i\varphi}{2}\right) & 0\\ 0 & \exp\left(-\frac{i\varphi}{2}\right)\end{pmatrix}\begin{bmatrix}u\\ d\end{bmatrix} = \begin{bmatrix}e^{i\varphi/2}u\\ e^{-i\varphi/2}d\end{bmatrix}
$$

then we get that

$$
\begin{aligned}
\langle\Psi|\,\sigma_x\,|\Psi\rangle &= \begin{bmatrix}e^{-i\varphi/2}u^*(r) & e^{i\varphi/2}d^*(r)\end{bmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{bmatrix}e^{i\varphi/2}u(r)\\ e^{-i\varphi/2}d(r)\end{bmatrix} = e^{-i\varphi}u^*(r)d(r) + e^{i\varphi}d^*(r)u(r) \\
&= \operatorname{Re}(e^{-i\varphi}u^*d) + i\operatorname{Im}(e^{-i\varphi}u^*d) + \operatorname{Re}(e^{-i\varphi}u^*d) - i\operatorname{Im}(e^{-i\varphi}u^*d) \\
&= 2\operatorname{Re}(e^{-i\varphi}u^*d)
\end{aligned}
$$

and

$$\begin{aligned}\langle\Psi|\,\sigma_y\,|\Psi\rangle &= \begin{bmatrix} e^{-i\varphi/2}u^*(r) & e^{i\varphi/2}d^*(r)\end{bmatrix}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{bmatrix} e^{i\varphi/2}u(r)\\ e^{-i\varphi/2}d(r)\end{bmatrix} = -ie^{i\varphi}u^*(r)d(r) + ie^{i\varphi}d^*(r)u(r)\\ &= -i\,\mathrm{Re}(e^{-i\varphi}u^*d) + \mathrm{Im}(e^{-i\varphi}u^*d) + i\,\mathrm{Re}(e^{-i\varphi}u^*d) + \mathrm{Im}(e^{-i\varphi}u^*d)\\ &= 2\,\mathrm{Im}(e^{-i\varphi}u^*d)\end{aligned}$$

lastly,

$$\begin{aligned}\langle\Psi|\,\sigma_z\,|\Psi\rangle = \begin{bmatrix} e^{-i\varphi/2}u^*(r) & e^{i\varphi/2}d^*(r)\end{bmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{bmatrix} e^{i\varphi/2}u(r)\\ e^{-i\varphi/2}d(r)\end{bmatrix} &= u^*(r)u(r) - d^*(r)d(r)\\ &= |u|^2 - |d|^2\end{aligned}$$

and hence then expectation value of the spin operator on this spinsor is given by

$$\langle\Psi'|\,\hat{S}\,|\Psi'\rangle = \frac{\hbar}{2}\left[2\,\mathrm{Re}(e^{-i\varphi}u^*d)u_x + 2\,\mathrm{Im}(e^{-i\varphi}u^*d)u_y + (|u|^2 - |d|^2)u_z\right]$$

Part e

Suppose that $u^*d = a + bi$ then $a = \frac{1}{2}S_x$ and $b = \frac{1}{2}S_y$ and we have that

$$e^{-i\varphi}u^*d = (a+bi)(\cos(i\varphi) - i\sin(\varphi)) = a\cos(\varphi) + b\sin(\varphi) + i\,(b\cos(\varphi) - a\sin(\varphi))$$

thus

$$S'_x = 2\,\mathrm{Re}(e^{-i\varphi}u^*d) = S_x\cos(\varphi) + S_y\sin(\varphi)$$

and

$$S'_y = 2\,\mathrm{Im}(e^{-i\varphi}u^*d) = S_y\cos(\varphi) - S_x\sin(\varphi)$$

and clearly

$$S'_z = S_z$$

Part f

From the change of coordinates in Part e, we have that $\exp\left(i\varphi\frac{\hat{S}_z}{\hbar}\right)$ is a clockwise rotation about the z-axis by angle φ.

Problem 4.2

Part a

Recall that

$$\chi_\uparrow = \begin{bmatrix}1\\0\end{bmatrix} \quad \text{and} \quad \chi_\downarrow = \begin{bmatrix}0\\1\end{bmatrix}$$

and note that

$$\chi_\uparrow \otimes \chi_\uparrow = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}$$

$$\chi_\uparrow \otimes \chi_\downarrow = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\1\\0\\0\end{bmatrix}$$

$$\chi_\downarrow \otimes \chi_\uparrow = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\1\\0\end{bmatrix}$$

$$\chi_\downarrow \otimes \chi_\downarrow = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

and hence we see that

$$\psi(\mathbf{r}_1, \mathbf{r}_2; 1)\chi_\uparrow \otimes \chi_\uparrow + \psi(\mathbf{r}_1, \mathbf{r}_2; 2)\chi_\uparrow \otimes \chi_\downarrow + \psi(\mathbf{r}_1, \mathbf{r}_2; 3)\chi_\downarrow \otimes \chi_\uparrow + \psi(\mathbf{r}_1, \mathbf{r}_2; 4)\chi_\downarrow \otimes \chi_\downarrow$$

becomes

$$\psi(\mathbf{r}_1, \mathbf{r}_2; 1)\begin{bmatrix}1\\0\\0\\0\end{bmatrix} + \psi(\mathbf{r}_1, \mathbf{r}_2; 2)\begin{bmatrix}0\\1\\0\\0\end{bmatrix} + \psi(\mathbf{r}_1, \mathbf{r}_2; 3)\begin{bmatrix}0\\0\\1\\0\end{bmatrix} + \psi(\mathbf{r}_1, \mathbf{r}_2; 4)\begin{bmatrix}0\\0\\0\\1\end{bmatrix} = \begin{bmatrix}\psi(\mathbf{r}_1, \mathbf{r}_2; 1)\\\psi(\mathbf{r}_1, \mathbf{r}_2; 2)\\\psi(\mathbf{r}_1, \mathbf{r}_2; 3)\\\psi(\mathbf{r}_1, \mathbf{r}_2; 4)\end{bmatrix}$$

Part b

To compute $(\hat{S}_{\text{tot}}))_z$ we compute

$$(\hat{S}_{\text{tot}})_z = S_z \otimes I + I \otimes S_z = \frac{\hbar}{2}\left(\sigma_z \otimes I + I \otimes \sigma_z\right)$$

then we have that

$$\sigma_z \otimes I = \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} \otimes \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} = \begin{pmatrix}1 & 0 & 0 & 0\\0 & 1 & 0 & 0\\0 & 0 & -1 & 0\\0 & 0 & 0 & -1\end{pmatrix}$$

$$I \otimes \sigma_z = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} \otimes \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} = \begin{pmatrix}1 & 0 & 0 & 0\\0 & -1 & 0 & 0\\0 & 0 & 1 & 0\\0 & 0 & 0 & -1\end{pmatrix}$$

then we have that

$$(\hat{S}_{\text{tot}})_z = \frac{\hbar}{2}\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Note that doing a similar process for $(S_{\text{tot}})_x$ and $(S_{\text{tot}})_y$ we get that

$$(\hat{S}_{\text{tot}})_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

$$(\hat{S}_{\text{tot}})_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i & -i & 0 \\ i & 0 & 0 & -i \\ i & 0 & 0 & -i \\ 0 & i & i & 0 \end{pmatrix}$$

so then we have that

$$S_{\text{tot}}^2 = (\hat{S}_{\text{tot}})_x^2 + (\hat{S}_{\text{tot}})_y^2 + (\hat{S}_{\text{tot}})_z^2 = \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix}$$

Part c

Consider

$$\begin{aligned} \Psi_1 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\uparrow \otimes \chi_\uparrow \\ \Psi_2 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\uparrow \otimes \chi_\downarrow \\ \Psi_3 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\downarrow \otimes \chi_\uparrow \\ \Psi_4 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\downarrow \otimes \chi_\downarrow \end{aligned}$$

Then we have that

$$\begin{aligned} \langle \Psi_1 | S_{\text{tot}}^2 | \Psi_1 \rangle &= \int \begin{bmatrix} f^*(\mathbf{r}_1, \mathbf{r}_2) & 0 & 0 & 0 \end{bmatrix} \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix} \begin{bmatrix} f(\mathbf{r}_1, \mathbf{r}_2) \\ 0 \\ 0 \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \int 2\hbar^2 |f(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = 2\hbar^2 \end{aligned}$$

$$\begin{aligned} \langle \Psi_2 | S_{\text{tot}}^2 | \Psi_2 \rangle &= \int \begin{bmatrix} 0 & f^*(\mathbf{r}_1, \mathbf{r}_2) & 0 & 0 \end{bmatrix} \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix} \begin{bmatrix} 0 \\ f(\mathbf{r}_1, \mathbf{r}_2) \\ 0 \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \int \hbar^2 |f(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = \hbar^2 \end{aligned}$$

$$\langle\Psi_3|\,S^2_{\text{tot}}\,|\Psi_3\rangle = \int \begin{bmatrix} 0 & 0 & f^*(\mathbf{r}_1,\mathbf{r}_2) & 0 \end{bmatrix} \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix} \begin{bmatrix} 0 \\ 0 \\ f(\mathbf{r}_1,\mathbf{r}_2) \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \int \hbar^2 |f(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = \hbar^2$$

$$\langle\Psi_4|\,S^2_{\text{tot}}\,|\Psi_4\rangle = \int \begin{bmatrix} 0 & 0 & 0 & f^*(\mathbf{r}_1,\mathbf{r}_2) \end{bmatrix} \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ f(\mathbf{r}_1,\mathbf{r}_2) \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \int 2\hbar^2 |f(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = 2\hbar^2$$

Part d

$$\langle\Psi_1|\,(S_{\text{tot}})_z\,|\Psi_1\rangle = \int \begin{bmatrix} f^*(\mathbf{r}_1,\mathbf{r}_2) & 0 & 0 & 0 \end{bmatrix} \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{bmatrix} f(\mathbf{r}_1,\mathbf{r}_2) \\ 0 \\ 0 \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \int \hbar |f(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = \hbar$$

$$\langle\Psi_2|\,(S_{\text{tot}})_z\,|\Psi_2\rangle = \int \begin{bmatrix} 0 & f^*(\mathbf{r}_1,\mathbf{r}_2) & 0 & 0 \end{bmatrix} \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{bmatrix} 0 \\ f(\mathbf{r}_1,\mathbf{r}_2) \\ 0 \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= 0$$

$$\langle\Psi_3|\,(S_{\text{tot}})_z\,|\Psi_3\rangle = \int \begin{bmatrix} 0 & 0 & f^*(\mathbf{r}_1,\mathbf{r}_2) & 0 \end{bmatrix} \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{bmatrix} 0 \\ 0 \\ f(\mathbf{r}_1,\mathbf{r}_2) \\ 0 \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= 0$$

$$\langle\Psi_4|\,(S_{\text{tot}})_z\,|\Psi_4\rangle = \int \begin{bmatrix} 0 & 0 & 0 & f^*(\mathbf{r}_1,\mathbf{r}_2) \end{bmatrix} \begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ f(\mathbf{r}_1,\mathbf{r}_2) \end{bmatrix} d\mathbf{r}_1 d\mathbf{r}_2$$
$$= -\int \hbar |f(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = -\hbar$$

Part e

For $\Psi(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_1, \mathbf{r}_2)\chi_1 \otimes \chi_2$ to be antisymmetric, we require that $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$. This means that we require

$$f(\mathbf{r}_1, \mathbf{r}_2)\chi_1 \otimes \chi_2 = -f(\mathbf{r}_2, \mathbf{r}_1)\chi_2 \otimes \chi_1$$

that is if $\chi_1 \otimes \chi_2 = \chi_2 \otimes \chi_1$ (i.e. $\chi_1 = \chi_2$) then we have that we require $f(\mathbf{r}_1, \mathbf{r}_2) = -f(\mathbf{r}_2, \mathbf{r}_1)$, that is f must be antisymmetric.

Part f

We wish to show that the two–electron spinors

$$\Psi_a(\mathbf{r}_1, \mathbf{r}_2) = f_a(\mathbf{r}_1, \mathbf{r}_2)\Big(\chi_\uparrow \otimes \chi_\downarrow + \chi_\downarrow \otimes \chi_\uparrow\Big),$$

$$\Psi_s(\mathbf{r}_1, \mathbf{r}_2) = f_s(\mathbf{r}_1, \mathbf{r}_2)\Big(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow\Big),$$

fulfill Pauli's principle, swapping $\mathbf{r}_1$ with $\mathbf{r}_2$ yields

$$\Psi_a(\mathbf{r}_2, \mathbf{r}_1) = f_a(\mathbf{r}_2, \mathbf{r}_1) Bigl(\chi_\uparrow \otimes \chi_\downarrow + \chi_\downarrow \otimes \chi_\uparrow\Big) = -f(\mathbf{r}_1, \mathbf{r}_2)\Big(\chi_\uparrow \otimes \chi_\downarrow + \chi_\downarrow \otimes \chi_\uparrow\Big).$$

Thus, Ψ_a is antisymmetric under electron exchange. Similarly, under exchange we have

$$\Psi_s(\mathbf{r}_2, \mathbf{r}_1) = f_s(\mathbf{r}_2, \mathbf{r}_1)\Big(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow\Big).$$

Since f_s is symmetric, and recalling that the spin singlet is antisymmetric, we obtain

$$\Psi_s(\mathbf{r}_2, \mathbf{r}_1) = f_s(\mathbf{r}_1, \mathbf{r}_2)\Big[-\big(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow\big)\Big] = -f_s(\mathbf{r}_1, \mathbf{r}_2)\Big(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow\Big) = -\Psi_s(\mathbf{r}_1, \mathbf{r}_2).$$

Thus, Ψ_s is also antisymmetric. Thus the wavefunction satisfy

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_1, \mathbf{r}_2),$$

Part g

$$\begin{aligned}
\Psi_1 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\uparrow \otimes \chi_\uparrow \\
\Psi_2 &= f(\mathbf{r}_1, \mathbf{r}_2)\frac{1}{\sqrt{2}}(\chi_\uparrow \otimes \chi_\downarrow + \chi_\downarrow \otimes \chi_\uparrow) \\
\Psi_3 &= f(\mathbf{r}_1, \mathbf{r}_2)\chi_\downarrow \otimes \chi_\downarrow \\
\Psi_4 &= f(\mathbf{r}_1, \mathbf{r}_2)(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow)
\end{aligned}$$

then we see that

$$\begin{aligned}
\langle\Psi_1| (S_{tot})_z |\Psi_1\rangle &= \hbar \\
\langle\Psi_1| S_{tot}^2 |\Psi_1\rangle &= 2\hbar^2
\end{aligned}$$

and

$$\begin{aligned}\langle\Psi_2|\,(S_{tot})_z\,|\Psi_2\rangle &= 0 + 0 = 0\\ \langle\Psi_2|\,S_{tot}^2\,|\Psi_2\rangle &= \frac{2\hbar^2}{2} + \frac{2\hbar^2}{2} = 2\hbar^2\end{aligned}$$

and

$$\begin{aligned}\langle\Psi_3|\,(S_{tot})_z\,|\Psi_3\rangle &= -\hbar\\ \langle\Psi_3|\,S_{tot}^2\,|\Psi_3\rangle &= \frac{2\hbar^2}{2} + \frac{2\hbar^2}{2} = 2\hbar^2\end{aligned}$$

and lastly,

$$\begin{aligned}\langle\Psi_4|\,(S_{tot})_z\,|\Psi_4\rangle &= 0 - 0 = 0\\ \langle\Psi_4|\,S_{tot}^2\,|\Psi_4\rangle &= \frac{2\hbar^2}{2} - \frac{2\hbar^2}{2} = 0\end{aligned}$$

Problem 4.3

Part a

Consider the singlet spinor Slater determinant given by

$$\psi(1,2) = \phi(1)\phi(2)\frac{1}{\sqrt{2}}\left(\chi_\uparrow \otimes \chi_\downarrow - \chi_\downarrow \otimes \chi_\uparrow\right)$$

recall that

$$\chi_\uparrow \otimes \chi_\downarrow = \begin{bmatrix}0\\1\\0\\0\end{bmatrix} \quad \text{and} \quad \chi_\downarrow \otimes \chi_\uparrow = \begin{bmatrix}0\\0\\1\\0\end{bmatrix}$$

thus

$$\psi(1,2) = \phi(1)\phi(2)\frac{1}{\sqrt{2}}\left(\begin{bmatrix}0\\1\\0\\0\end{bmatrix} - \begin{bmatrix}0\\0\\1\\0\end{bmatrix}\right) = \phi(1)\phi(2)\frac{1}{\sqrt{2}}\begin{bmatrix}0\\1\\-1\\0\end{bmatrix}$$

similarly we find that

$$\psi(2,1) = \phi(1)\phi(2)\frac{1}{\sqrt{2}}\left(\chi_\downarrow \otimes \chi_\uparrow - \chi_\uparrow \otimes \chi_\downarrow\right) = \phi(1)\phi(2)\frac{1}{\sqrt{2}}\begin{bmatrix}0\\-1\\1\\0\end{bmatrix} = -\psi(1,2)$$

hence ψ is anti-symmetric.

Part b

For ψ to be normalized we require that,

$$\langle\psi|\psi\rangle = \int d1d2\psi^*\psi = \int d1d2|\phi(1)|^2|\phi(2)|^2 = \left(\int dr|\phi(r)|^2\right)^2 = 1$$

which implies that

$$\int dr|\phi(r)|^2 = 1$$

hence for ψ to be normalized, ϕ must also be normalized.

Part c

Suppose we have the following Hamiltonian,

$$\hat{H} = \hat{H}_0(r) + \hat{H}_0(r') + \frac{\beta}{|r-r'|}$$

where

$$\hat{H}_0(r) = -\frac{\hbar^2\nabla^2}{2m} - \frac{2\beta}{|r|} \quad \text{and} \quad \beta = \frac{e^2}{4\pi\epsilon_0}$$

then we see that

$$\langle\psi|\,\hat{H}\,|\psi\rangle = \langle\psi|\,\hat{H}_0(r)\,|\psi\rangle + \langle\psi|\,\hat{H}_0(r')\,|\psi\rangle + \beta\,\langle\psi|\,\frac{1}{r-r'}\,|\psi\rangle$$

additionally we see that

$$\begin{aligned}
\langle\psi|\,\hat{H}_0(r)\,|\psi\rangle &= \frac{1}{2}\int drdr'\begin{bmatrix} 0 & 1 & -1 & 0\end{bmatrix}\begin{bmatrix} 0 \\ 1 \\ -1 \\ 0\end{bmatrix}|\phi(r')|^2\phi^*(r)\hat{H}_0(r)\phi(r) \\
&= \int drdr'|\phi(r')|^2\phi^*(r)\hat{H}_0(r)\phi(r) = \int dr'|\phi(r')|^2\int dr\phi^*(r)\hat{H}_0(r)\phi(r) \\
&= \int dr\phi^*(r)\hat{H}_0(r)\phi(r)
\end{aligned}$$

we can do a similar process for $\langle\psi|\,\hat{H}_0(r')\,|\psi\rangle$ and we get that

$$\langle\psi|\,\hat{H}_0(r)\,|\psi\rangle + \langle\psi|\,\hat{H}_0(r')\,|\psi\rangle = 2\int dr\phi^*(r)\hat{H}_0(r)\phi(r)$$

lastly for the last term we get that

$$\begin{aligned}
\beta\,\langle\psi|\,\frac{1}{r-r'}\,|\psi\rangle &= \frac{\beta}{2}\int drdr'\frac{\phi^*(r)\phi(r)\phi^*(r')\phi(r')}{|r-r'|}\begin{bmatrix} 0 & 1 & -1 & 0\end{bmatrix}\begin{bmatrix} 0 \\ 1 \\ -1 \\ 0\end{bmatrix} \\
&= \beta\int\int drdr'\frac{\phi^*(r)\phi(r)\phi^*(r')\phi(r')}{|r-r'|}
\end{aligned}$$

hence we have that

$$E = \langle\psi|\,\hat{H}\,|\psi\rangle = 2\int dr\phi^*(r)\hat{H}_0(r)\phi(r) + \beta\int\int drdr'\frac{\phi^*(r)\phi(r)\phi^*(r')\phi(r')}{|r-r'|}$$

Part d

Recall that we can write the minimization of E with respect to $\phi^*(r)$ subject to the normalization constraint via the Lagrangian as,

$$L = E - \lambda\left(\int dr|\phi(r)|^2 - 1\right)$$

and we wish to find $\phi(r)$ such that

$$\frac{\delta L}{\delta\phi^*(r)} = \frac{\delta E}{\delta\phi^*(r)} - \frac{\delta}{\delta\phi^*(r)}\lambda\left(\int dr\phi^*(r)\phi(r) - 1\right) = 0$$

Note that for the first term, we have that

$$\begin{aligned}
&\frac{d}{d\epsilon}|_{\epsilon=0}\left(2\int dr[\phi(r)+\epsilon\delta(r'-r)]^*\hat{H}_0(r)\phi(r)\right) = 2\hat{H}_0(r)\phi(r)\\
&\frac{d}{d\epsilon}|_{\epsilon=0}\left(\beta\int drdr'\frac{[\phi(r)+\epsilon\delta(r-r')]^*\phi(r)[\phi(r')+\epsilon\delta(r'-r)]^*\phi(r')}{|r-r'|}\right)\\
&= \beta\int\int drdr'\frac{\delta(r-r')\phi(r)\phi^*(r')\phi(r')}{|r-r'|} + \beta\int\int drdr'\frac{\phi^*(r)\phi(r)\delta(r'-r)\phi(r')}{|r-r'|}\\
&= \beta\int\int drdr'\frac{\delta(r-r')\phi(r)\phi^*(r')\phi(r')}{|r-r'|} + \beta\int\int drdr'\frac{\phi^*(r)\phi(r)\delta(r'-r)\phi(r')}{|r-r'|}\\
&= 2\beta\phi(r)\int dr'\frac{|\phi(r')|^2}{|r-r'|}
\end{aligned}$$

lastly we get that

$$\frac{\delta}{\delta\phi^*(r)}\lambda\left(\int dr\phi^*(r)\phi(r) - 1\right) = \lambda\frac{d}{d\epsilon}|_{\epsilon=0}\int dr[\phi(r)+\epsilon\delta(r-r')]^*\phi(r) = \lambda\phi(r)$$

so then by re-arranging terms we get that

$$\hat{H}_0(r)\phi(r) + \beta\phi(r)\int dr'\frac{|\phi(r')|^2}{|r-r'|} = \frac{\lambda}{2}\phi(r) = \epsilon\phi(r)$$

or

$$-\frac{\hbar^2}{2m}\nabla^2\phi(r) + \left[-\frac{2e^2}{4\pi\epsilon_0|r|} + \int dr'\frac{e^2|\phi(r')|^2}{4\pi\epsilon_0|r-r'|}\right]\phi(r) = \epsilon\phi(r)$$

Part e

Consider the effective potential,

$$V_{\text{eff}}(r) = -\frac{2e^2}{4\pi\epsilon_0|r|} + \int dr' \frac{e^2|\phi(r')|^2}{4\pi\epsilon_0|r-r'|}$$

Now if we consider the case where $|r| \to 0$, we see that

$$\frac{2e^2}{4\pi\epsilon_0|r|} \to \infty \quad \text{and} \quad \int dr' \frac{e^2|\phi(r')|^2}{4\pi\epsilon_0|r-r'|} \to \int dr' \frac{e^2|\phi(r')|^2}{4\pi\epsilon_0|r'|} < \infty$$

hence for sufficiently small r we have that the right-hand term dominates and hence the potential behaves as

$$V_{\text{eff}}(r) \sim -\frac{Ze^2}{4\pi\epsilon_0|r|}$$

where $Z = 2$. Now if $|r| \to \infty$ we have that for sufficiently large r, $|r - r'| \sim |r|$ and hence

$$V_{\text{eff}}(r) \sim -\frac{2e^2}{4\pi\epsilon_0|r|} + \int dr' \frac{e^2|\phi(r')|^2}{4\pi\epsilon_0|r|} = -\frac{e^2}{4\pi\epsilon_0|r|}\left(2 - \int dr'|\phi(r')|^2\right) \sim -\frac{e^2}{4\pi\epsilon_0|r|}$$

and hence

$$V_{\text{eff}}(r) \sim -\frac{Ze^2}{4\pi\epsilon_0|r|}$$

with $Z = 1$.

Part f

Suppose we have the normalized wavefunction:

$$\phi(r; Z) = \frac{a_0^{-3/2}}{\sqrt{\pi}} Z^{3/2} \exp\left(-Z\frac{|r|}{a_0}\right)$$

in order to compute the total energy E as function of Z, first recall that

$$E = 2\int dr \phi^*(r)\hat{H}_0(r)\phi(r) + \beta \int\int dr dr' \frac{\phi^*(r)\phi(r)\phi^*(r')\phi(r')}{|r-r'|}$$

for the first term we have that

$$\hat{H}_0(r)\phi(r) = \hat{H}_0(r) = -\frac{\hbar^2\nabla^2\phi(r)}{2m} - \frac{2\beta}{|r|}\phi(r) = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\phi(r) - \frac{2\beta}{|r|}\phi(r)$$

Note that

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\frac{a_0^{-3/2}}{\sqrt{\pi}}Z^{3/2}\exp\left(-Z\frac{|r|}{a_0}\right) &= -\frac{a_0^{-3/2}Z^{3/2}\hbar^2}{2m\sqrt{\pi}}\frac{1}{r^2}\frac{\partial}{\partial r}\left(-r^2\frac{Z}{a_0}\exp(-Zr/a_0)\right) \\
&= -\frac{a_0^{-5/2}Z^{5/2}\hbar^2}{2m\sqrt{\pi}}\left(-\frac{2}{r}\exp(-Zr/a_0) + \frac{Z}{a_0}\exp(-Zr/a_0)\right) \\
&= -\frac{a_0^{-5/2}Z^{5/2}\hbar^2}{2m\sqrt{\pi}}\exp(-Zr/a_0)\left(-\frac{2}{r} + \frac{Z}{a_0}\right)
\end{aligned}$$

then we see that

$$2\int dr\phi^*(r)\left[-\frac{h^2}{2m}\nabla^2\right]\phi(r) = 8\pi\left(-\frac{a_0^{-5/2}Z^{5/2}\hbar^2}{2m\sqrt{\pi}}\right)\frac{a^{-3/2}Z^{3/2}}{\sqrt{\pi}}\int drr^2e^{-2Zr/z_0}\left(-\frac{2}{r}+\frac{Z}{a_0}\right)$$
$$= -\frac{4a_0^{-4}Z^4\hbar^2}{m}\left(-\frac{a_0^2}{2Z^2}+\frac{a_0^2}{4Z^2}\right)$$
$$= Z^2E_{Ha}$$

and,

$$2\int dr\phi^*(r)\left[\frac{2\beta}{|r|}\right]\phi(r) = 16\beta\pi\left(\frac{a_0^{-3}Z^3}{\pi}\right)\int drre^{-2Zr/a_0}$$
$$= 16\beta a_0^{-3}Z^3\frac{a_0^2}{4Z^2}$$
$$= 4\beta a_0^{-1}Z$$
$$= 4ZE_{Ha}$$

For the second term, we have that by setting $u = \frac{2Z}{a_0}r$ and similarly for r', we get that

$$\beta\int\int drdr'\frac{\phi^*(r)\phi(r)\phi^*(r')\phi(r')}{|r-r'|} = \beta\left(\frac{Z^6a_0^{-6}}{\pi^2}\right)\left(\frac{a_0}{2Z}\right)^6\frac{2Z}{a_0}\frac{a_0}{2Z}\int du\int du'\frac{\exp(-|u|-|u'|)}{|u-u'|}$$
$$= \beta\frac{5}{8}Z = \frac{5}{8}ZE_{Ha}$$

Therefore

$$E = Z^2E_{Ha} - 4ZE_{Ha} + Z\frac{5}{8}E_{Ha} = Z\left(Z-\frac{27}{8}\right)E_{Ha}$$

Part g

To find the minimum energy we compute

$$\frac{dE}{dZ} = 0 \implies \left(Z-\frac{27}{8}\right)E_{Ha} + ZE_{Ha} = 0 \implies Z = \frac{27}{16}$$

so the minimum energy is

$$E_{\min} \approx -2.84765625E_{Ha}$$

Part h

Z represents the effective charge felt by an electron.

Part i

Since the two electrons are indistinguishable, we get that

$$n(r) = 2\int |\psi(r, r_2)|^2\, dr_2 = 2\int\, dr_2 |\phi(r)|^2 |\phi(r_2)|^2$$
$$= 2|\phi(r)|^2 = 2\frac{\left(\frac{27}{16}\right)^3}{\pi a_0^3} \exp\left(\frac{-52r}{16a_0}\right)$$

Part j

for $Z = 2$, we get

$$n(r) = 2\int |\psi(r, r_2)|^2\, dr_2 = 2\int\, dr_2 |\phi(r)|^2 |\phi(r_2)|^2$$
$$= 2|\phi(r)|^2 = 2\frac{8}{\pi a_0^3} \exp\left(\frac{-4r}{a_0}\right)$$

CSE_389D/ps_4/density(1).png

Figure 4.1. $4\pi r^2 n(r)$ vs r

```python
# -*- coding: utf-8 -*-
"""Untitled33.ipynb

Automatically generated by Colab.

Original file is located at
    https://colab.research.google.com/drive/1oGEH790QVb9VMQUKuzFAa6FCdJAyAs3O
"""

import numpy as np
import matplotlib.pyplot as plt

def n(r,Z):
  a = 1
  return 8 * (r**2) * (Z**3)/(a**3) * np.exp(-2*Z*r/a)

r = np.linspace(0,10,1000)

plt.plot(r,n(r,27/16), label=r"$Z_{opt}$")
plt.plot(r,n(r,2), label=r"$Z = 2$")
plt.xlabel(r"$r$")
plt.ylabel(r"$4 \pi r^2n(r)$")
```

```
plt.grid()
plt.legend()
plt.savefig("density.png")
```