Assignment8

Zhuan Li

October 2020

1 EX8

1.1 Normalization factor

We have

$$
\begin{aligned}
&\int_{-\infty}^{\infty} |\psi(\vec{r})|^2 \mathrm{d}^3 r = \int_{-\infty}^{\infty} N_{s,a}^2 (\phi_1(\vec{r}) \pm \phi_2(\vec{r}))^2 \mathrm{d}^3 r \\
&= \int_{-\infty}^{\infty} N_{s,a}^2 (\phi_1(\vec{r})^2 \pm 2\phi_1(\vec{r})\phi_2(\vec{r}) + \phi_2(\vec{r})^2) \mathrm{d}^3 r \\
&= N_{s,a}^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x,y,z) e^{x+y+z} \mathrm{d}x\mathrm{d}y\mathrm{d}z \\
&= 8N_{s,a}^2 \int_{0}^{\infty}\int_{0}^{\infty}\int_{0}^{\infty} f(x,y,z) e^{-x-y-z} \mathrm{d}x\mathrm{d}y\mathrm{d}z \\
&= 8N_{s,a}^2 I_{s,a}
\end{aligned}
$$

where $f(x,y,z) = (\phi_1(\vec{r})^2 \pm 2\phi_1(\vec{r})\phi_2(\vec{r}) + \phi_2(\vec{r})^2)e^{x+y+z}$. So we can choose the probability distribution $\rho(x,y,z) = e^{-x-y-z}$, and then calculate the average value of $f(x,y,z)$. Therefore we can get the normalization factor $N_{s,a} = \sqrt{1/(8I_{s,a})}$. Then we can plot the normalization factors as the function of the distance d. The results are showed in follow:

When the distance to the infinity, the two atoms become independent, therefore, the normalization factor of symmetry and anti-symmetry wave functions approach to $1/\sqrt{2}$.

1.2 Energy

We have the Schrodinger equation:

$$
\begin{aligned}
&H\psi_{s,a} = E_{s,a}\psi_{s,a} \\
&= (-\frac{1}{2}\nabla^2 - \frac{1}{|\vec{r} + \hat{z}d/2|} - \frac{1}{|\vec{r} - \hat{z}d/2|})\psi_{s,a} \\
&= N_{s,a}^2 \psi_{s,a}
\end{aligned}
$$

Therefore we have $E_{s,a} = N_{s,a}^2$. And here the normalization factors can be obtained from previous subsection.

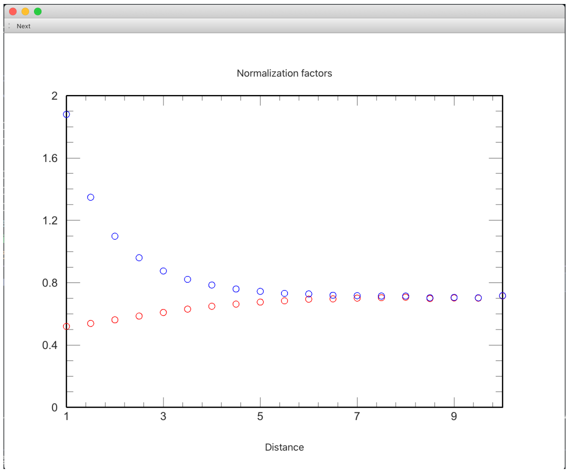

Figure 2: Normalization factors.

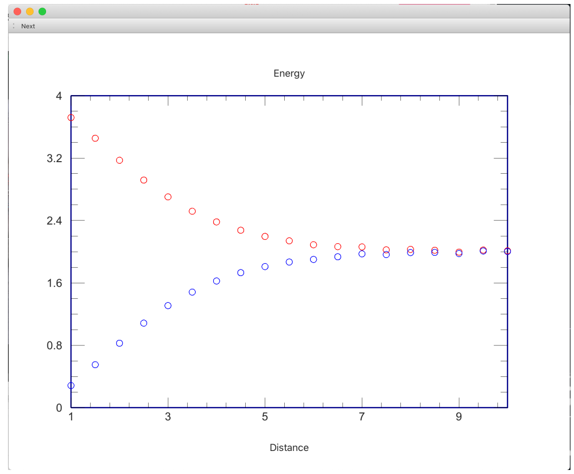

Figure 3: Energy of the system

The energy of symmetric wave function (red circle) decreases with the increase of distance d, while the energy of the anti-symmetric wave function (blue circle) increases with the increase of distance d. And as $d \to \infty$, the energy approach to 2, which is the energy for two isolated atom.

2 EX9

3 EX15

3.1

We have:

$$\sigma_1 = \sqrt{\frac{\bar{f^2} - \bar{f}^2}{N}} = \sqrt{\frac{\int_0^1 (e^x - 1)^2/(e-1)^2 \mathrm{d}x - I^2}{N}}$$
$$= \left(\sqrt{\frac{e^2 - 4e + 5}{2(e-1)^2}} - I^2 \right) / \sqrt{N} = \frac{0.286}{\sqrt{N}}$$

If we want to achieve 1% accuracy, we have $0.286/\sqrt{N} < 0.01 \Rightarrow N > 817$.

3.2

We can choose $\rho(x) = 2x$, then we have:

$$\bar{f^2} = \int_0^1 \left(\frac{(e^x - 1)}{2x(e-1)} \right)^2 2x \mathrm{d}x = 0.1775$$

Therefore we have $\sigma_2 = \sqrt{0.177489 - 0.17474}/\sqrt{N} = 0.0524/\sqrt{N}$. If we want to achieve 1% accuracy, we have $0.0524/\sqrt{N} < 0.01 \Rightarrow N > 26$.

Here I calculated the integral by using two weight functions with different N for 50 times, and I plot the average error in the diagram below:

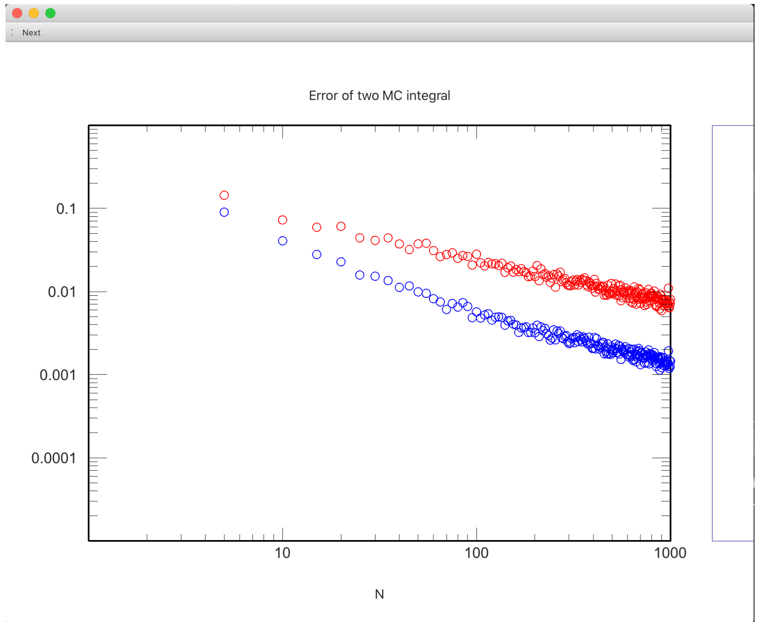

Figure 3: Error of two different weight functions: $w = 1$(red circle) and $w = x$(blue circle).

We can read from the diagram that the slop of the two line is around 1/2 which consist with the formula. When $N > 30$, the accuracy for the second weight function is smaller that 1%. And when $N > 800$, the accuracy for the first weight function is smaller that 1%.

3.3

We have the ratio of variance:

$$\frac{\sigma_1^2}{\sigma_2^2} = \frac{\bar{f_1^2} - I^2}{\bar{f_2^2} - I^2} = \frac{\Pi \bar{f_1^2}(x_i) - \Pi I_i^2}{\Pi \bar{f_2^2}(x_i) - \Pi I_i^2}$$

In the limit of $D \to \infty$, we have $\Pi I_i = I_i^{2D} = 0$. Now we have:

$$\frac{\sigma_1^2}{\sigma_2^2} = \prod \frac{\bar{f_1^2}(x_i)}{\bar{f_2^2}(x_i)} = \left(\frac{\bar{f_1^2}(x_i)}{\bar{f_2^2}(x_i)} \right)^D = 1.4464^D = 10^{0.16D}$$