积分公式[1]

$$\iint d^3x_1 d^3x_2 \frac{\exp\left[-2Z\left(r_1+r_2\right)\right]}{r_{12}} = \frac{5\pi^2}{8Z^5} \tag{1}$$

其中

$$\frac{1}{r_{12}} = \frac{1}{\left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|} = \begin{cases} \dfrac{1}{r_2}\sum\limits_{l=0}\left(\dfrac{r_1}{r_2}\right)^l P_l\left(\cos\theta_{12}\right) & r_1 < r_2 \\ \dfrac{1}{r_1}\sum\limits_{l=0}\left(\dfrac{r_2}{r_1}\right)^l P_l\left(\cos\theta_{12}\right) & r_1 > r_2 \end{cases} \tag{2}$$

及

$$P_l\left(\cos\theta_{12}\right) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_l^{m*}\left(\theta_1,\varphi_1\right) Y_l^m\left(\theta_2,\varphi_2\right) \tag{3}$$

代入积分公式(1)左侧

$$I\left(Z\right) = \iint d^3x_1 d^3x_2 \frac{\exp\left[-2Z\left(r_1+r_2\right)\right]}{r_{12}} \tag{4}$$

考虑到 Y_l^m 积分的正交归一性，式(2)各项中只有$l=0$项对$I(Z)$有贡献，由此得出

$$\begin{aligned} I\left(Z\right) = {} & \left(4\pi\right)^2 \int_0^\infty r_2^2 dr_2 \exp\left(-2Zr_2\right) \\ & \times\left[\frac{1}{r_2}\int_0^\infty r_1^2 \exp\left(-2Zr_1\right) dr_1 + \int_0^\infty r_1 \exp\left(-2Zr_1\right) dr_1\right] \end{aligned} \tag{5}$$

考虑积分

$$F\left(n,a,b\right) = \int_a^b e^{-x} x^n dx \tag{6}$$

采用分步积分，有

$$\begin{aligned} F\left(n,a,b\right) &= -\left[e^{-x}x^n\right]_a^b + n\int_a^b e^{-x}x^{n-1}dx = -\left[e^{-x}x^n\right]_a^b + nF\left(n-1,a,b\right) \\ &= -\left[e^{-x}x^n\right]_a^b + n\left[-\left[e^{-x}x^{n-1}\right]_a^b + \left(n-1\right)F\left(n-2,a,b\right)\right] \\ &= -\left[e^{-x}\left(x^n + nx^{n-1}\right)\right]_a^b + n\left(n-1\right)F\left(n-2,a,b\right) \\ &= -\left[e^{-x}\left(x^n + nx^{n-1} + n\left(n-1\right)x^{n-2}\right)\right]_a^b + n\left(n-1\right)\left(n-2\right)F\left(n-3,a,b\right) \\ &= \cdots \left[\sum_{i=0}^{n-1}\frac{n!}{\left(n-i\right)!}x^{n-i}\right]_a^b + n!F\left(0,a,b\right) \\ &= -\left[e^{-x}\sum_{i=0}^{n-1}\frac{n!}{\left(n-i\right)!}x^{n-i}\right]_a^b + n!\left[-e^{-x}\right]_a^b = -\left[e^{-x}\sum_{i=0}^{n}\frac{n!}{\left(n-i\right)!}x^{n-i}\right]_a^b \end{aligned} \tag{7}$$

因而

$$F\left(n,0,b\right)=n!\text{-}e^{-b}\sum_{i=0}^{n}\frac{n!}{\left(n-i\right)!}b^{n-i} \tag{8}$$

$$F\left(n,a,\infty\right)=e^{-a}\sum_{i=0}^{n}\frac{n!}{\left(n-i\right)!}a^{n-i} \tag{9}$$

$$F\left(n,0,\infty\right)=n! \tag{10}$$

于是

$$\begin{aligned}
I\left(Z\right)&=\left(4\pi\right)^2\int_0^\infty r_2^2dr_2\exp\left(-2Zr_2\right)\\
&\quad\times\left\{\frac{1}{r_2}\frac{1}{\left(2Z\right)^3}\left[2-\exp\left(-2Zr_2\right)\left[\left(2Zr_2\right)^2+2\times\left(2Zr_2\right)+2\right]\right]\right.\\
&\quad\left.+\frac{1}{\left(2Z\right)^2}\exp\left(-2Zr_2\right)\left[\left(2Zr_2\right)+1\right]\right\}\\
&=\frac{4\pi^2}{Z^3}\left\{\int_0^\infty r_2^2\exp\left(-2Zr_2\right)dr_2-Z\int_0^\infty r_2^2\exp\left(-4Zr_2\right)dr_2\right.\\
&\quad\left.-\int_0^\infty r_2\exp\left(-4Zr_2\right)dr_2\right.\\
&=\frac{4\pi^2}{Z^3}\left[\frac{Z}{\left(2Z\right)^3}\times2-\frac{Z}{\left(4Z\right)^3}\times2-\frac{1}{\left(4Z\right)^2}\right]\\
&=\frac{4\pi^2}{Z^3}\times\frac{5}{32Z^2}=5\pi^2/8Z^5
\end{aligned} \tag{11}$$

[1] 量子力学. 卷 I/曾谨言著.——4 版。——北京：科学出版社，2007（现代物理丛书）.ISBN：978-7-03-018139-8. P365