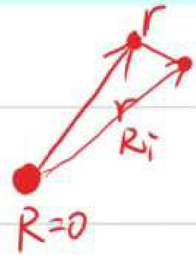
$$\iiint_E f(x,y,z)\,dV = \int_\delta^\gamma \int_\alpha^\beta \int_a^b \rho^2 \sin\varphi\ f(\rho\sin\varphi\cos\theta, \rho\sin\varphi\sin\theta, \rho\cos\varphi)\ d\rho\, d\theta\, d\varphi$$



$$= \sum_A \langle \chi_i | V_A | \chi_j \rangle$$

$$\langle \chi_i | V | \chi_j \rangle = \sum_R \langle \chi_i | V_R | \chi_j \rangle$$

其中 $\langle \chi_i | V_R | \chi_j \rangle = \iiint_{>R_N} \chi_i \left(-\frac{1}{|r-R|}\chi_j\right) dxdydz + \iiint_{<R_N} \chi_i V \chi_j\, dxdydz.$

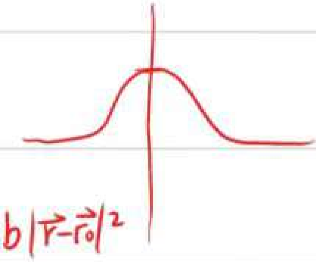
$$= \int_0^\infty -r e^{-b(\vec{r}-\vec{R}_i)^2} = -b\left[(r-R\cos\varphi)^2 + R\sin^2\varphi\right]$$

$-R_N$·被截函数$(r=0)$

↓

R_N很小，采取优等积分

取势原子中心为零点：



$$\chi_i \chi_j = (x-x_i)^m (x-x_j)^n (y-y_i)^{m'} (y-y_j)^{n'} e^{-b|\vec{r}-\vec{r}_0|^2}$$

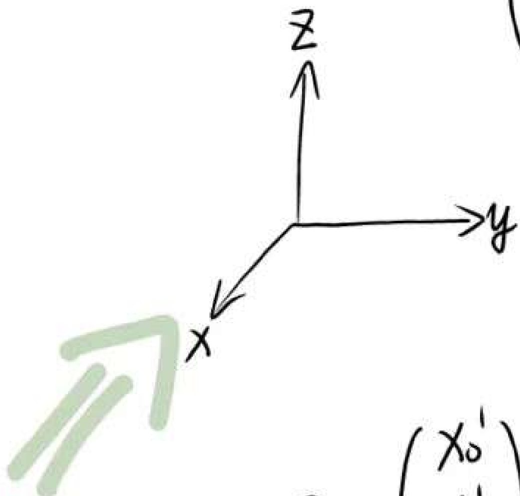
⇓ 旋转使$\vec{r}_0$为z方向.

$$\int_0^\infty \Big[-r(r\sin\varphi\cos\theta - x_i)^m (r\sin\varphi\cos\theta - x_j)^n (r\sin\varphi\sin\theta - y_i)^{m'} (r\sin\varphi\sin\theta - y_j)^{n'}$$

$$e^{-b(r-R\cos\varphi)^2} e^{R\sin^2\varphi} \Big]$$

$-R_N$·被积$(r=0)$
放外面.

$$\begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} \xrightarrow{\text{归一化}} \begin{pmatrix} x_0' \\ y_0' \\ z_0' \end{pmatrix}$$



取势原子中心零点

↓

高斯函数乘积

↓

取指数上的坐标为z轴方向

↓

换球坐标

↓

积$r \in [0, \infty]$

↓

积φ

↓

积θ

↓

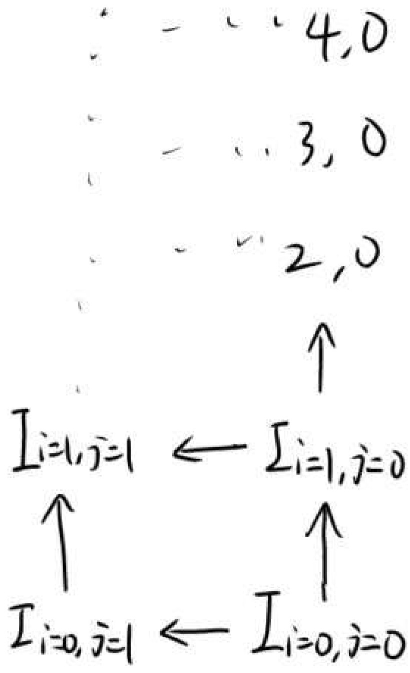
各因子积分加和乘系数.

↓

挖去R_{vdW}小洞.

$$R \begin{pmatrix} x_0' \\ y_0' \\ z_0' \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$R = \begin{pmatrix} y_0' & -x_0' & 0 \\ 0 & -z_0' & y_0' \\ x_0' & y_0' & z_0' \end{pmatrix}$$



$$\int_{-\infty}^{\infty} (x-x_j)^n e^{-b(x-x_0)^2} dx$$

$$I_1 = \int (x-x_j) e^{-b(x-x_0)^2} dx$$

$$= -\frac{1}{2b} e^{-b(x-x_0)^2} \Big|_{-\infty}^{+\infty} + (x_0-x_j) \int e^{-b(x-x_0)^2} dx.$$

$$= (x_j-x_0) I_0$$

$$I_2 = \int (x-x_j)^2 e^{-b(x-x_0)^2} dx$$

$$= -\frac{1}{2b} (x-x_j) e^{-b(x-x_0)^2} \Big|_{-\infty}^{+\infty} + (x_0-x_j) I_1 + \frac{1}{2b} I_0$$

$$= (x_0-x_j) I_1 + \frac{1}{2b} I_0.$$

$$I_3 = \int (x-x_j)^3 e^{-b(x-x_0)^2} dx$$

$$= -\frac{1}{2b} (x-x_j)^2 e^{-b(x-x_0)^2} \Big|_{-\infty}^{+\infty} + (x_0-x_j) I_2 + \frac{1}{2b} \cdot 2 I_1$$

$$= (x_0-x_j) I_2 + \frac{1}{2b} \cdot 2 I_1$$

$$\int_{-\infty}^{\infty}(x-x_i)^m(x-x_j)^n e^{-b(x-x_0)^2}\,dx$$

$$I_{j=n,i=1}=\int(x-x_i)(x-x_j)^n e^{-b(x-x_0)^2}\,dx$$

$$=-\frac{1}{2b}(x-x_j)^n e^{-b(x-x_0)^2}\Big|_{-\infty}^{\infty}+(x_0-x_i)I_{j=n,i=0}+\frac{1}{2b}nI_{j=n-1,i=0}$$

$$=(x_0-x_i)I_{j=n,i=0}+\frac{1}{2b}nI_{j=n-1,i=0}$$

$$I_{j=n,i=2}=\int(x-x_i)^2(x-x_j)^n e^{-b(x-x_0)^2}\,dx$$

$$=-\frac{1}{2b}(x-x_i)(x-x_j)^n e^{-b(x-x_0)^2}\Big|_{-\infty}^{\infty}+(x_0-x_i)I_{j=n,i=1}+\frac{1}{2b}I_{j=n,i=0}$$

$$+\frac{1}{2b}nI_{j=n-1,i=1}$$

$$=(x_0-x_i)I_{j=n,i=1}+\frac{1}{2b}I_{j=n,i=0}+\frac{1}{2b}nI_{j=n-1,i=1}$$

$$I_{j=n,i=3}=\int(x-x_i)^3(x-x_j)^n e^{-b(x-x_0)^2}\,dx$$

$$=-\frac{1}{2b}(x-x_i)^2(x-x_j)^n e^{-b(x-x_0)^2}\Big|_{-\infty}^{\infty}+(x_0-x_i)I_{j=n,i=2}+\frac{1}{2b}2I_{j=n,i=1}$$

$$+\frac{1}{2b}nI_{j=n-1,i=2}$$

$$=(x_0-x_i)I_{j=n,i=2}+\frac{1}{2b}2I_{j=n,i=1}+\frac{1}{2b}nI_{j=n-1,i=2}$$

各降一阶

$$\int_0^{\infty} (a_n x - x_j)^n e^{-b(x-x_0)^2} dx$$

最高到a_n

$$I_1 = \int (a_n x - x_j) e^{-b(x-x_0)^2} dx$$

$$= -\frac{a_n}{2b} e^{-b(x-x_0)^2} \Big|_0^{\infty} + (a_n x_0 - x_j) \int e^{-b(x-x_0)^2} dx.$$

$$= \frac{-a_n}{2b} e^{-b x_0^2} + (a_n x_j - x_0) I_0$$

最高到a_n^2

$$I_2 = \int (a_n x - x_j)^2 e^{-b(x-x_0)^2} dx$$

$$= -\frac{a_n}{2b} (a_n x - x_j) e^{-b(x-x_0)^2} \Big|_0^{+\infty} + (a_n x_0 - x_j) I_1 + \frac{a_n^2}{2b} I_0$$

$$= \frac{a_n}{2b} x_j e^{-b x_0^2} + (a_n x_0 - x_j) I_1 + \frac{a_n^2}{2b} I_0$$

最高到a_n^3

$$I_3 = \int (a_n x - x_j)^3 e^{-b(x-x_0)^2} dx$$

$$= -\frac{a_n}{2b} (a_n x - x_j)^2 e^{-b(x-x_0)^2} \Big|_0^{+\infty} + (a_n x_0 - x_j) I_2 + \frac{a_n^2}{2b} \cdot 2 I_1$$

$$= \frac{-a_n}{2b} x_j^2 e^{-b x_0^2} + (a_n x_0 - x_j) I_2 + \frac{a_n^2}{2b} \cdot 2 I_1$$

$$\int_0^{\infty}(a_m x-x_i)^m(a_n x-x_j)^n e^{-b(x-x_0)^2}dx$$

最高到$a_m a_n^n$

$$I_{j=n,i=1}=\int(a_m x-x_i)(a_n x-x_j)^n e^{-b(x-x_0)^2}dx$$

$$=-\frac{a_m}{2b}(a_n x-x_j)^n e^{-b(x-x_0)^2}\Big|_0^{\infty}+(a_m x_0-x_i)I_{j=n,i=0}+\frac{a_m a_n}{2b}nI_{j=n-1,i=0}$$

$$=-\frac{a_m}{2b}(-x_j)^n e^{-bx_0^2}+(a_m x_0-x_i)I_{j=n,i=0}+\frac{n\cdot a_m a_n}{2b}nI_{j=n-1,i=0}$$

最高到$a_m^2 a_n^n$

$$I_{j=n,i=2}=\int(a_m x-x_i)^2(a_n x-x_j)^n e^{-b(x-x_0)^2}dx$$

$$=-\frac{a_m}{2b}(a_m x-x_i)(a_n x-x_j)^n e^{-b(x-x_0)^2}\Big|_0^{\infty}+(a_m x_0-x_i)I_{j=n,i=1}+\frac{a_m\cdot a_m}{2b}I_{j=n,i=0}$$

$$+\frac{a_m a_n}{2b}nI_{j=n-1,i=1}$$

$$=\frac{a_m}{2b}x_i(-x_j)^n e^{-bx_0^2}+(a_m x_0-x_i)I_{j=n,i=1}+\frac{a_m\cdot a_m}{2b}I_{j=n,i=0}+\frac{a_m a_n}{2b}nI_{j=n-1,i=1}$$

最高到$a_m^3 a_n^n$

$$I_{j=n,i=3}=\int(a_m x-x_i)^3(a_n x-x_j)^n e^{-b(x-x_0)^2}dx$$

$$=-\frac{a_m}{2b}(a_m x-x_i)^2(a_n x-x_j)^n e^{-b(x-x_0)^2}\Big|_0^{\infty}+(a_m x_0-x_i)I_{j=n,i=2}+\frac{a_m a_m}{2b}2I_{j=n,i=1}$$

$$+\frac{a_m a_n}{2b}nI_{j=n-1,i=2}$$

$$=-\frac{a_m}{2b}x_i^2(-x_j)^n e^{-bx_0^2}+(a_m x_0-x_i)I_{j=n,i=2}+\frac{a_m a_m}{2b}2I_{j=n,i=1}+\frac{a_m a_n}{2b}nI_{j=n-1,i=2}$$