Integral Evaluation

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1 Equations

Q1: Gaussian Integrals:

$$R_k = \int_{-\infty}^{\infty} dx x^k e^{-ax^2} \quad NB: I = \int_{-\infty}^{\infty} dx x^{2l} e^{-2ax^2} = \frac{(2l-1)!!\sqrt{\pi}}{(4a)^l\sqrt{2\alpha}}$$

The integral above can be evaluated using the Leibniz rule or it can be evaluated by substituting $k = 0, 2, 4, \ldots$ for even functions; for odd numbers of $k = 1, 3, 5, \ldots$, the integral is zero.
when $k = 0, R_k = \int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\pi/a}$
when $k = 2; R_k = \int_{-\infty}^{\infty} dx x^2 e^{-ax^2} = \frac{\sqrt{\pi}}{2a^{3/2}}$
when $k = 4; R_k = \int_{-\infty}^{\infty} dx x^4 e^{-ax^2} = \frac{3\sqrt{\pi}}{4a^{5/2}}$
when $k = 6; R_k = \int_{-\infty}^{\infty} dx x^6 e^{-ax^2} = \frac{15\sqrt{\pi}}{8a^{7/2}}$

Following the pattern, a relation can be drawn for a general expression for the integral

$$R_k = \int_{-\infty}^{\infty} x^k e^{-ax^2} dx = \frac{[k-1]!!\sqrt{\pi}}{[2\alpha]^{k/2}\sqrt{a}} = \sqrt{\frac{\pi}{\alpha}} \cdot \frac{(k-1)!!}{(2a)^{k/2}}$$

Q2. Using the Gaussian Product Theorem for s-type Gaussians

$$G(r;\alpha,A)G(\gamma,\beta,B) = KG(r;\alpha+\beta,P), \quad K = K_x K_y K_z$$

$$K_x = \exp\left(\frac{-\alpha\beta}{\alpha+\beta}(A_x - B_x)^2\right) \quad P_x = \frac{\alpha A_x + \beta B_x}{\alpha+\beta}$$

$$K_y = \exp\left(\frac{-\alpha\beta}{\alpha+\beta}(A_y - B_y)^2\right) \quad P_y = \frac{\alpha A_y + \beta B_y}{\alpha+\beta}$$

$$K_z = \exp\left(\frac{-\alpha\beta}{\alpha+\beta}(A_z - B_z)^2\right) \quad P_z = \frac{\alpha A_z + \beta B_z}{\alpha+\beta}$$

where $K = K_x K_y K_z$

$$\rightarrow K = \exp\left(\frac{-\alpha\beta}{\alpha+\beta}\left[(A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2\right]\right)$$

In, $\alpha, A\rangle \equiv G(\gamma; n, \alpha, R) = (r_x - R_x)^{n_x}(r_y - R_y)^{n_y}(\gamma_z - R_z)^{n_z}\exp\left(-\alpha|\gamma - R|^2\right)$

Comparing to

$$= (r_x - A_x)^{n_x}(r_y - AA_y)^{n_y}(r_z - Az)^{n_z}\exp\left(-\alpha|\gamma - A|^2\right) \times (r_x - Bx)^{m_x}(r_y - B_y)^{m_y}(r_z - B_z)^{m_z}\exp\left(-\beta|\gamma - B|^2\right)$$

$$= (r_x - A_x)^{n_x}(r_x - B_x)^{m_x}(r_y - A_y)^{n_y}(r_y - B_y)^{m_y}(r_z - A_z)^{n_z}(r_z - B_z)^{m_z}\exp\left(-\alpha|\gamma - A|^2\right)\exp\left(-\beta|\gamma - B|^2\right)$$

Solving the exponential function, $2 - \alpha|r - A|^2 - \beta|r - B|^2$

$$2 - \alpha\left|r^2 - 2Ar + A^2\right| - \beta\left|r^2 - 2Br + B^2\right|$$

$$= -\alpha|r|^2 + 2\alpha|A||r| - \alpha|A|^2 - \beta|r|^2 + 2\beta|B||r| - \beta|B|^2$$

$$= -(\alpha+\beta)|r|^2 + 2|r|(\alpha|A| + \beta|B|) - \alpha|A|^2 - \beta|B|^2$$

$$= -(\alpha+\beta)|r|^2 + \frac{2|r|(\alpha+\beta)(\alpha|A| + \beta|B|)}{(\alpha+\beta)} - (\alpha+\beta)\left|\frac{\alpha A + \beta B}{\alpha+\beta}\right|^2 + (\alpha+\beta)\left|\frac{\alpha A + \beta B}{\alpha+\beta}\right|^2 - \left(\alpha|A|^2 + \beta|B|^2\right)$$

where $P = \dfrac{\alpha A + \beta B}{\alpha + \beta}$

$= -(\alpha+\beta)|r|^2 + 2|r|(\alpha+\beta)p - (\alpha+\beta)|p|^2 - (\alpha+\beta)|p|^2 - \left(\alpha|A|^2 + \beta|B|^2\right)$

$= -(\alpha+\beta)\underbrace{(|r|^2 - 2|r||P| + |P|^2)} - \underbrace{(\alpha+\beta)|P|^2 - \left(\alpha|A|^2 + \beta|B|^2\right)}$

$-(\alpha+\beta)|r-P|^2 \quad - \dfrac{\alpha\beta}{(\alpha+\beta)}\left(|A-B|^2\right)$

$G(r; n, \alpha, A)G(r; m, \beta, B) = (r_x - A_x)^{n_x}(r_x - B_x)^{m_x}(r_y - A_y)^{n_y}(r_y - B_y)^{m_y}(r_2 - A_z)^{n_2}(r_z - B_z)^{m_2}$
$e^{(\alpha+\beta)|r-p|^2 - \frac{\alpha\beta}{a+\beta}(|A-B)^2)}$

$\langle n, \alpha, A \mid m, \beta, B\rangle = \displaystyle\int (r_x - A_x)^{n_x}(r_x - B_x)^{m_x}(r_y - A_y)^{n_y}(r_y - B_y)^{m_y}(r_2 - A_z)^{n_2}(r_z - B_z)^{m_2}$
$e^{-(\alpha+\beta)|r-P|^2} \cdot e^{\frac{-\alpha\beta}{\alpha+\beta}\left(|A-B|^2\right)}$

because, $I_x = \int (r_x - A_x)^{n_x}(r_x - B_x)^{m_x} \exp\left(-(\alpha+\beta)(r_x - P_x)^2\right)$

$$\langle n, \alpha, A \mid m, \beta, B\rangle = I_x I_y I_z \exp\left(\frac{-\alpha\beta}{\alpha+\beta}\left(|A-B|^2\right)\right).$$

Rewrite $r_x - A_x$ as $(r_x - P_x)+$ $(P_x - A_x)$and we will use the binomial expansion

$$(a+b)^c = \sum_{d=0}^{c} a^{c-d}b^d \begin{pmatrix} c \\ d \end{pmatrix} \text{ to show that}$$

$$(r_x - A_x)^{n_x}(\gamma_x - \beta_x)^{m_x} = \sum_{i=0}^{n_x}(P_x - A_x)^{n_x - i}\sum_{j=0}^{m_x}(P_x - \beta_x)^{m_x - j}(m_j)(r_x - P_x)^{i+j}$$

$[\{[p_x - n_x) + (r_x - p_x)^{n_x}\}\{(p_x - B_x) + (r_x - P_x)\}^{m_x}]$

$$= \sum_{i=0}^{n_x}(P_x - A_x)^{n_x - i}\left(\ n_x - P_x\ \right)\begin{pmatrix} n_x \\ i \end{pmatrix}\sum_{j=0}^{m_x}(P_n - B_x)^{m_x - j}(r_x - P_x)^j\begin{pmatrix} m_x \\ j \end{pmatrix}$$

$$= \sum_{i=0}^{n_x}(P_x - A_x)^{n_x - i}\begin{pmatrix} n_x \\ i \end{pmatrix}\sum_{j=0}^{m_n}(P_x - B_x)^{m_x - j}\begin{pmatrix} x_n \\ j \end{pmatrix}$$

$$= \sum_{i=0}^{n_x}\sum_{j=0}^{m_x}\begin{pmatrix} n_x \\ i \end{pmatrix}\begin{pmatrix} m_x \\ j \end{pmatrix}(P_x - A_x)^{n_x - j}(P_x - B_x)^j(r_x - P_x)^{i+j}$$

Finally, using eqn 2: $\int_{-\infty}^{\infty} x^k e^{-ax^2}dx$ to derive an expression for I_x.

$$I_x = \int \underbrace{(r_x - A_x)^{m_x}(r_x - B_x)^{m_x}}_{111}\exp\left(-(a+\beta)(r_x - P_x)^2\right)$$

$$I_x = \sum_{i=0}^{n_x}\sum_{j=0}^{m_x}\begin{pmatrix} n_x \\ i \end{pmatrix}\begin{pmatrix} m_x \\ j \end{pmatrix}(P_x - A_x)^{n_x - i}(P_x - B_x)^{m_x - j}\int_{-\infty}^{\infty}(r_x - P_x)^{i+j}\exp\left(-(\alpha+\beta)(r_x - P_x)^2\right)$$

$$I_x = \sum_{i=0}^{n_x}\sum_{j=0}^{m_x}\begin{pmatrix} n_x \\ i \end{pmatrix}\begin{pmatrix} m_x \\ j \end{pmatrix}(P_x - A_x)^{n_x - i}(P_x - B_x)^{m_x - j}\sqrt{\frac{\pi}{\alpha+\beta}} \cdot \frac{(i+j-1)!!}{[2(\alpha+\beta)]^{\frac{(i+j)}{2}}}$$

$$I_x = \sqrt{\frac{\pi}{\alpha+\beta}}\sum_{i=0}^{n_x}\sum_{j=0}^{m_x}\begin{pmatrix} n_x \\ i \end{pmatrix}\begin{pmatrix} m_x \\ j \end{pmatrix}\frac{(i+j-1)!!}{[2(\alpha+\beta)]^{(i+j)/2}} \cdot (p_x - A_x)^{n_x - i}(p_x - B_x)^{m_x - j}$$

Q3: The kinetic energy integrals over s-type Gaussians.

$$\rightarrow |0,\alpha,A\rangle = \exp\left(-a|r-A|^2\right)$$

$$\frac{\partial^2}{\partial r_x^2}\left(\exp\left(-a|r-A|^2\right) = \frac{\partial}{\partial r_x}\left(\frac{\partial}{\partial x_x}\exp\left(-\alpha|r-A|^2\right)\right)\right.$$

$$=\frac{\partial}{\partial r_x}\left(-2\alpha(\gamma-A)e^{-\alpha(r-A)^2}\right)$$

Using the chain rule to evaluate the differential expression

$$\frac{\partial}{\partial r_x}\left(-2\alpha\left(r_x-A\right)\exp\left(-\alpha\left|r_x-A\right|^2\right)\right)$$

$$=-2\alpha\cdot\frac{\partial}{\partial r_x}\left[\left(r_x-A\right)\exp\left(-\alpha\left|r_x-A\right|^2\right)\right]$$

$$=-2\alpha\cdot\left(e^{-\left(\alpha|r_x-A|^2\right)}\cdot\frac{\partial}{\partial r_x}\left(r_x-A\right)+\left(r_x-A\right)\cdot\frac{\partial}{\partial r_x}\exp\left(-\alpha\left|r_x-A\right|^2\right)\right)$$

$$=-2\alpha\left[e^{-\left(\alpha|r_x-A|^2\right)}+\left(r_x-A\right)\cdot-2\alpha\left(r_x-A\right)\exp\left(-\alpha\left|r_x-A\right|^2\right)\right]$$

$$=-2\alpha\exp\left(-\alpha\left|r_x-A\right|^2\right)+4\alpha^2\left(r_x-A\right)^2\exp\left(-a\left|r_x-A\right|^2\right)$$

$$\text{NB; }\left(r_x-A\right)^2\exp\left(-\alpha\left|r_x-A\right|^2\right)\equiv|2x,\alpha,A\rangle$$

$$\exp\left(-\alpha\left|r_x-A\right|^2\right)\equiv|0,\alpha,A\rangle$$

$$\text{Hence, }\frac{\partial^2}{\partial r_x^2}|0,\alpha,A\rangle=-2\alpha\exp\left(-\alpha\left|r_x-A\right|^2\right)+4\alpha^2\left(r_x-A\right)^2\exp\left(-a\left|r_x-A\right|^2\right)$$

$$z-2\alpha|0,\alpha,A\rangle+4\alpha^2|2x,\alpha,A\rangle$$

Express the matrix element of the kinetic energy operator over s-type Gaussians,

$$\langle 0,\alpha,A|\hat{T}|O,\beta,B\rangle,\text{ where }\hat{T}=-\frac{1}{2}\left(\frac{\partial^2}{\partial r_x^2}+\frac{\partial^2}{\partial r_y^2}+\frac{\partial^2}{\partial r_z^2}\right)$$

$$\left\langle 0,\alpha,A\left|-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right|0,\beta,B\right\rangle=-\frac{1}{2}\sum_{izx,y,z}\left\langle 0,\alpha,A\left|\frac{\partial^2}{\partial r_i^2}\right|0,\beta,B\right\rangle$$

$$=-\frac{1}{2}\left[\left\langle 0,\alpha,A\left|\frac{\partial^2}{\partial x^2}\right|0,\beta,B\right\rangle+\left\langle 0,\alpha,A\left|\frac{\partial^2}{\partial y^2}\right|O,\beta,B\right\rangle+\left\langle 0,\alpha,A\left|\frac{\partial^2}{\partial z^2}\right|0,\beta,B\right\rangle\right]$$

$$I_x=-\left\langle 0,\alpha,A\left|\frac{1-\partial^2}{\partial}\partial x^2\right|O,\beta,B\right\rangle=\beta\langle 0,\alpha,A\mid 0,\beta,B\rangle+2\beta^2\langle 0,\alpha,A\mid 2x,\beta,B\rangle$$

$$=\beta\left[e^{-\frac{\alpha\beta}{\alpha+\beta}}|A-B|^2\cdot\sqrt{\frac{\pi}{\alpha+\beta}}\right]-2\beta^2\left[e^{-\frac{\alpha\beta}{\alpha+\beta}|A-B|^2}\cdot\frac{1}{2(\alpha+\beta)}\sqrt{\frac{\pi}{\alpha+\beta}}\right]$$

For the general expression

$$\left\langle 0,\alpha,A\left|-\tfrac{1}{2}\nabla^2\right|2,\phi,B\right\rangle=\tfrac{\alpha\beta}{(\alpha+\beta)}\left[3-\tfrac{2\alpha\beta}{(\alpha+\beta)}|A-B|^2\right][\pi/(\alpha+\beta)]^{3/2}\exp\left[\tfrac{-\alpha\beta}{\alpha+\beta}|A-\beta|^2\right]$$

Q4 : Nuclear attraction:

The auxiliary Hermite Coulomb integral $R_{tuv}^n(p,\mathbf{P},\mathbf{C})$ handles Coulomb interaction between a Gaussian charge distributi centered at $\mathbf{P}$ and a nuclei centered at $\mathbf{C}$.

$$\begin{aligned}
R_{t+1,u,v}^n &= tR_{t-1,u,v}^{n+1}+X_{PC}R_{t,u,v}^{n+1}\\
R_{t,u+1,v}^n &= uR_{t,u-1,v}^{n+1}+Y_{PC}R_{t,u,v}^{n+1}\\
R_{t,u,v+1}^n &= vR_{t,u,v-1}^{n+1}+Z_{PC}R_{t,u,v}^{n+1}\\
R_{0,0,0}^n &= (-2p)^nF_n\left(pR_{PC}^2\right)
\end{aligned}$$

where, $F_n(T)$ is the Boys function

$$F_n(T)=\int_0^1\exp\left(-Tx^2\right)x^{2n}dx$$

Now that we have a the Coulomb auxiliary Hermite integrals R^n_{tuv}, we can form the nuclear attraction integrals with respect to a given nucleus centered at C, $V_{ab}(C)$, via the expression

$$V_{ab}(C) = \frac{2\pi}{p} \sum_{t,u,v}^{i+j+1,k+l+1,m+n+1} E^{ij}_t E^{kl}_u E^{mn}_v R^0_{tuv}(p, \mathbf{P}, \mathbf{C})$$

Q5 : Two-electron Integral

We will use Hermite Gaussians, to express express S_{ab} as

$$\begin{aligned} S_{ab} &= \int \sum_{t=0}^{i+j} E^{ij}_t \Lambda_t dx \\ &= \sum_{t=0}^{i+j} E^{ij}_t \int \Lambda_t dx \\ &= \sum_{t=0}^{i+j} E^{ij}_t \delta_{t0} \sqrt{\frac{\pi}{p}} \\ &= E^{ij}_0 \sqrt{\frac{\pi}{p}} \end{aligned}$$

where

E^{ij}_t are expansion coefficients (that will be determined recursively) and Λ_t is the Hermite Gaussian overlap of two Gaussians a and b. This can be defined using the following recursive definitions

$$\begin{aligned} E^{ij}_t &= \frac{1}{2p} E^{i,j-1}_{t-1} + \frac{qQ_x}{\beta} E^{i,j-1}_t + (t+1) E^{i,j-1}_{t+1} \\ E^{ij}_t &= \frac{1}{2p} E^{i-1,j}_{t-1} - \frac{qQ_x}{\alpha} E^{i-1,j}_t + (t+1) E^{i-1,j}_{t+1} \\ E^{00}_0 &= K_{AB} \\ E^{ij}_t &= 0 \quad \text{if} \quad t < 0, \quad \text{or} \quad t > i+j \end{aligned}$$

In terms of Hermite integrals, the two-electron integral can be written as

$$g_{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{t,u,v}^{i+j+1,k+l+1,m+n+1} E^{ij}_t E^{kl}_u E^{mn}_v \sum_{\tau,\nu,\phi}^{i'+j'+1,k'+l'+1,m'+n'+1} E^{i'j'}_\tau E^{k'l'}_\nu E^{m'n'}_\phi (-1)^{\tau+\nu+\phi} R^0_{t+\tau,u+\nu,v+\phi}(p, q, \mathbf{P}, \mathbf{Q})$$