AIMP integral

coulomb potential: M_1, M_2
projection operator
exchange potential: spectral representation operator

1 M_1 coulomb potential

M_1 coulomb potential: s-type GTO times nuclear attraction

$$\hat{O}_{M_1} = \sum_{\zeta}^{nucleus} \hat{O}^{\zeta}_{M_1} = \sum_{\zeta}^{nuc} \frac{1}{|\vec{r}-\vec{R}_\zeta|} \sum_{I\in\zeta} A_I e^{-\alpha_I|\vec{r}-\vec{R}_\zeta|^2}$$

$$\langle\chi_a| \frac{1}{r_{M_1}} \sum_I A_I e^{-\alpha_I r^2_{M_1}} |\chi_b\rangle = \sum_I A_I \iiint_{-\infty}^{+\infty} x_A^{l_i} y_A^{m_i} z_A^{n_i} e^{-\alpha_i r_A^2} \left[\frac{e^{-\alpha_I r^2_{M_1}}}{r_{M_1}}\right] x_B^{l_j} y_B^{m_j} z_B^{n_j} e^{-\alpha_j r_B^2} d^3r$$

$$\iiint_{-\infty}^{+\infty} x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2} \left[\frac{e^{-\alpha_3 r^2_{M_1}}}{r_{M_1}}\right] x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_2 r_B^2} d^3r$$

$$\text{laplace transform: } \tfrac{1}{r} = \tfrac{2}{\sqrt{\pi}} \int_0^\infty du e^{-u^2 r^2}$$

$$\text{1st GPT:} \vec{C} = \tfrac{\alpha_1\vec{A}+\alpha_2\vec{B}}{\alpha_1 2},\ \alpha_{12} = \alpha_1+\alpha_2$$

$$= e^{\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} \frac{2}{\sqrt{\pi}} \int_0^\infty du \iiint_{-\infty}^{+\infty} d^3r x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_{12} r_C^2} e^{-(u^2+\alpha_3) r^2_{M_1}}$$

$$\text{2nd GPT: } \vec{D} = \tfrac{\alpha_{12}\vec{C}+(u^2+\alpha_3)\vec{M}_1}{\alpha_{123}+u^2}$$

$$= e^{\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} \frac{2}{\sqrt{\pi}} \int_0^\infty du \iiint_{-\infty}^{+\infty} d^3r x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\frac{\alpha_{12}(u^2+\alpha_3)}{\alpha_{123}+u^2}|\overrightarrow{M_1C}|^2} e^{(\alpha_{123}+u^2) r_D^2}$$

$$t^2 = \tfrac{u^2}{\alpha_{123}+u^2},\ du = \tfrac{\sqrt{\alpha_{123}}}{(1-t^2)^{3/2}} dt$$

$$= e^{\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} e^{-\frac{\alpha_{12}\alpha_3}{\alpha_{123}}|\overrightarrow{M_1C}|^2} \frac{2\sqrt{\alpha_{123}}}{\sqrt{\pi}} \int_0^1 \frac{dt}{(1-t^2)^{3/2}} \iiint d^3r x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\frac{\alpha_{123}}{1-t^2} r_D^2} e^{-\frac{\alpha_{12}^2}{\alpha_{123}}|\overrightarrow{M_1C}|^2 t^2}$$

$$I_x(l_1,l_2,t) = \frac{1}{\sqrt{1-t^2}} \int_{-\infty}^{+\infty} dx x_A^{l_1} x_B^{l_2} e^{-\frac{\alpha_{123}}{1-t^2} x_D^2}$$

$$X = \tfrac{\alpha_{12}^2}{\alpha_{123}}|\overrightarrow{M_1C}|^2,\ E_{AB} = e^{\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2},\ E_{M_1C} = e^{-\frac{\alpha_{12}\alpha_3}{\alpha_{123}}|\overrightarrow{M_1C}|^2}$$

$$= E_{AB}E_{M_1C} \frac{2\sqrt{\alpha_{123}}}{\sqrt{\pi}} \int_0^1 I_x(l_1,l_2,t) I_y(m_1,m_2,t) I_z(n_1,n_2,t) e^{-Xt^2} dt$$

$$= E_{AB}E_{M_1C} \frac{2\sqrt{\alpha_{123}}}{\sqrt{\pi}} \sum_{p=1}^{N_p} \omega_p I_x(t_p) I_y(t_p) I_z(t_p)$$

HRR:
$I_x(l_1,l_2,t) = I_x(l_1+1,l_2-1,t) + (A_x-B_x) I_x(l_1,l_2-1,t)$
VRR:
$I_x(l_1,0,t) = (D_x-A_x) I_x(l_1-1,0,t) + \frac{(l_1-1)(1-t^2)}{2\alpha_{123}} I_x(l_2,0,t)$
$D_x - A_x = t^2(M_{1x}-C_x) + (C_x-A_x)$
$I_x(1,0,t) = (D_x-A_x) I_x(0,0,t)$
$I_x(0,0,t) = \sqrt{\frac{\pi}{\alpha_{123}}}$

2 M_2 coulomb potential

M_2 coulomb potential: s-type GTO

$$\hat{O}_{M_2} = \sum_{\zeta}^{nucleus} \hat{O}_{M_2}^{\zeta} = \sum_{\zeta}^{nuc} \sum_{J\in\zeta} A_J e^{-\alpha_J |\vec{r}-\vec{R}_\zeta|^2}$$

$$\langle\chi_a| \sum_J A_J e^{-\alpha_J r_{M_2}^2} |\chi_b\rangle = \sum_J A_J \iiint_{-\infty}^{+\infty} x_A^{l_i} y_A^{m_i} z_A^{n_i} e^{-\alpha_i r_A^2} \left[e^{-\alpha_I r_{M_2}^2}\right] x_B^{l_j} y_B^{m_j} z_B^{n_j} e^{-\alpha_j r_B^2} d^3r$$

$$\iiint x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2} e^{-\alpha_3 r_{M_2}^2} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_2 r_B^2} d^3r$$

$$\text{1st GPT: } \vec{C} = \tfrac{\alpha_1\vec{A}+\alpha_2\vec{B}}{\alpha_{12}}$$

$$= e^{-\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} \iiint x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_{12} r_C^2} e^{-\alpha_3 r_{M_2}^2} d^3r$$

$$\text{2nd GPT: } \vec{D} = \tfrac{\alpha_{12}\vec{C}+\alpha_3\vec{M}_2}{\alpha_{123}}$$

$$= e^{-\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} e^{\frac{\alpha_{12}\alpha_3}{\alpha_{123}}|\overrightarrow{CM_2}|^2} \iiint x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_{123} r_D^2} d^3r$$

$$I_x(l_1,l_2) = \textstyle\int_{-\infty}^{+\infty} x_A^{l_1} x_B^{l_2} e^{-\alpha_{123} x_D^2} dx$$
$$E_{AB} = e^{-\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2},\ E_{CM_2} = e^{\frac{\alpha_{12}\alpha_3}{\alpha_{123}}|\overrightarrow{CM_2}|^2}$$

$$= E_{AB} E_{CM_2} I_x(l_1,l_2) I_y(m_1,m_2) I_z(n_1,n_2)$$

HRR:
$I_x(l_1,l_2) = I_x(l_1+1,l_2-1) + (A_x - B_x) I_x(l_1,l_2-1)$
VRR:
$I_x(l_1,0) = (D_x - A_x) I_x(l_1-1,0) + \frac{l_1-1}{2\alpha_{123}} I_x(l_1-2,0)$
$I_x(1,0) = (D_x - A_x) I_x(0,0)$
$I_x(0,0) = \sqrt{\frac{\pi}{\alpha_{123}}}$

3 projection operator

$$\hat{P} = \sum_K B_K \left|\psi_K\right\rangle \left\langle\psi_K\right| = \sum_{\zeta}^{nuc} \sum_N \sum_{L=0}^{N-1} \sum_{l+m+n=L} B_{lmn}^{\zeta NL} \left|\psi_{lmn}^{\zeta NL}\right\rangle \left\langle\psi_{lmn}^{\zeta NL}\right|$$

$$= \sum_{\zeta}^{nuc} \sum_N \sum_{L=0}^{N-1} \sum_{l+m+n=L} B_{lmn}^{\zeta NL} \sum_{pq} (C_{lmn}^{\zeta NL})_p (C_{lmn}^{\zeta NL})_q^* \left|\phi_p^{\zeta}\right\rangle \left\langle\phi_q^{\zeta}\right|$$

atom orbital: $\{\chi_a\}$

$$\langle\chi_a|\phi_p\rangle = \iiint x_A^{l_1} y_A^{m_1} z_A^{n_1} e^{-\alpha_1 r_A^2} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_2 r_B^2} d^3r$$

GPT: $\vec{C} = \frac{\alpha_1\vec{A}+\alpha_2\vec{B}}{\alpha_{12}}$

$$= e^{-\frac{\alpha_1\alpha_2}{\alpha_{12}}|\overrightarrow{AB}|^2} \iiint x_A^{l_1} y_A^{m_1} z_A^{n_1} x_B^{l_2} y_B^{m_2} z_B^{n_2} e^{-\alpha_{12} r_C^2} d^3r$$

$$= E_A B I_x(l_1, l_2) I_y(m_1, m_2) I_z(n_1, n_2)$$

HRR and VRR:
$I_x(l_1, l_2) = I_x(l_1+1, l_2-1) + (A_x - B_x) I_x(l_1, l_2-1)$
$I_x(l_1, 0) = (C_x - A_x) I_x(l_1-1, 0) + \frac{l_1-1}{2\alpha_{12}} I_x(l_1-2, 0)$
$I_x(1, 0) = (C_x - A_x) I_x(0, 0)$
$I_x(0, 0) = \sqrt{\frac{\pi}{\alpha_{12}}}$

4 exchange potential

spectral representation operator:

$$\hat{I}^{SRO} = \sum_{ij} |i\rangle (S^{-1})_{ij} \langle j| \qquad S_{ij} = \langle i|j\rangle$$

$$\hat{O}^{SRO} = \hat{I}^{SRO}\hat{O}\hat{I}^{SRO} = \sum_{ijkl} |i\rangle (S^{-1})_{ij} \langle j|\hat{O}|k\rangle (S^{-1})_{kl} \langle l| = \sum_{il} |i\rangle (O^{SRO})_{il} \langle l|$$

$$(O^{SRO})_{il} = \sum_{jk} (S^{-1})_{ij} \langle j|\hat{O}|k\rangle (S^{-1})_{kl}$$

exchange operator:

$$\hat{O}_{exch} = \sum_{\zeta}^{nuc} \hat{O}^{\zeta}_{exch}$$

$$\hat{O}^{\zeta}_{exch} = \sum_{c\in\zeta} \langle \cdot\psi^{\zeta}_c|\psi^{\zeta}_c\cdot\rangle = \sum_{c\in\zeta}\sum_{N}\sum_{L=0}^{N-1}\sum_{l+m+n=L} \langle \cdot\psi^{\zeta NL}_{lmn}|\psi^{\zeta NL}_{lmn}\cdot\rangle$$

$$\begin{aligned}
\hat{O}^{SRO}_{exch} &= \sum_{\zeta}^{nuc} \hat{O}^{SRO,\zeta}_{exch} = \sum_{\zeta}^{nuc}\sum_{il} |\phi^{\zeta}_i\rangle (O^{SRO,\zeta}_{exch})_{il} \langle \phi^{\zeta}_l| \\
&= \sum_{\zeta}^{nuc}\sum_{il} |\phi^{\zeta}_i\rangle \left[\sum_{jk} (S^{-1})_{ij} \langle \phi^{\zeta}_j|\hat{O}^{\zeta}_{exch}|\phi^{\zeta}_k\rangle (S^{-1})_{kl}\right] \langle \phi^{\zeta}_l| \\
&= \sum_{\zeta}^{nuc}\sum_{il} |\phi^{\zeta}_i\rangle \left[\sum_{jk} (S^{-1})_{ij} \left[\sum_{c\in\zeta} \langle \phi^{\zeta}_j\psi^{\zeta}_c|\psi^{\zeta}_c\phi^{\zeta}_k\rangle\right] (S^{-1})_{kl}\right] \langle \phi^{\zeta}_l| \\
&= \sum_{\zeta}^{nuc}\sum_{il} |\phi^{\zeta}_i\rangle \left[\sum_{jk} (S^{-1})_{ij} \left[\sum_{c\in\zeta}\sum_{N}\sum_{L=0}^{N-1}\sum_{l+m+n=L} \langle \phi^{\zeta}_j\psi^{\zeta NL}_{lmn}|\psi^{\zeta NL}_{lmn}\phi^{\zeta}_k\rangle\right] (S^{-1})_{kl}\right] \langle \phi^{\zeta}_l| \\
&= \sum_{\zeta}^{nuc}\sum_{il} |\phi^{\zeta}_i\rangle \left[\sum_{jk} (S^{-1})_{ij} \left[\sum_{c\in\zeta}\sum_{N}\sum_{L=0}^{N-1}\sum_{l+m+n=L}\sum_{pq} (C^{\zeta NL}_{lmn})_p (C^{\zeta NL}_{lmn})^*_q \langle \phi^{\zeta}_j\phi^{\zeta}_p|\phi^{\zeta}_q\phi^{\zeta}_k\rangle\right] (S^{-1})_{kl}\right] \langle \phi^{\zeta}_l| \\
&= \sum_{\zeta}^{nuc}\sum_{il}\sum_{jk}\sum_{c\in\zeta}\sum_{N}\sum_{L=0}^{N-1}\sum_{l+m+n=L}\sum_{pq} |\phi^{\zeta}_i\rangle (S^{-1})_{ij} (C^{\zeta NL}_{lmn})_p (C^{\zeta NL}_{lmn})^*_q \langle \phi^{\zeta}_j\phi^{\zeta}_p|\phi^{\zeta}_q\phi^{\zeta}_k\rangle (S^{-1})_{kl} \langle \phi^{\zeta}_l|
\end{aligned}$$

$$\begin{aligned}
\langle \phi_j\phi_p|\phi_q\phi_k\rangle &= \iint d^3r_1 d^3r_2 \frac{1}{r_{12}} x_{1A}^{l_1+l_2} x_{2A}^{l_3+l_4} y_{1A}^{m_1+m_2} y_{2A}^{m_3+m_4} z_{1A}^{n_1+n_2} z_{2A}^{n_3+n_4} e^{-\alpha_{12} r_{1A}^2} e^{-\alpha_{34} r_{2A}^2} \\
&= \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-u^2|\vec{r}_1-\vec{r}_2|^2} du \iint d^3r_1 d^3r_2 x_{1A}^{l_1+l_2} x_{2A}^{l_3+l_4} y_{1A}^{m_1+m_2} y_{2A}^{m_3+m_4} z_{1A}^{n_1+n_2} z_{2A}^{n_3+n_4} e^{-\alpha_{12} r_{1A}^2} e^{-\alpha_{34} r_{2A}^2} \\
&= \frac{2}{\sqrt{\pi}} \int_0^{\infty} \tilde{I}_x(l_1+l_2,0,l_3+l_4,0;u)\tilde{I}_y(m_1+m_2,0,m_3+m_4,0;u)\tilde{I}_z(n_1+n_2,0,n_3+n_4,0;u) du
\end{aligned}$$

$$\tilde{I}_x(l_1+l_2,0,l_3+l_4,0;u) = \iint dx_1 dx_2 x_{1A}^{l_1+l_2} x_{2A}^{l_3+l_4} e^{-\alpha_{12} x_{1A}^2} e^{-\alpha_{34} x_{2A}^2} e^{-u^2(x_1-x_2)^2}$$

$$\begin{aligned}
\tilde{I}_x(0,0,0,0;u) &= \iint dx_1 dx_2 e^{-\alpha_{12} x_{1A}^2} e^{-\alpha_{34} x_{2A}^2} e^{-u^2(x_1-x_2)^2} \\
&= \int_{-\infty}^{+\infty} e^{-\alpha_{34}(x_2-A_x)^2} e^{-\frac{\alpha_{12}u^2}{\alpha_{12}+u^2}(x_2-A_x)^2} dx_2 \int_{-\infty}^{+\infty} e^{-(\alpha_{12}+u^2)(x_1-\frac{\alpha_{12}A_x+u^2x_2}{\alpha_{12}+u^2})^2} dx_1 \\
&= \sqrt{\frac{\pi}{\alpha_{12}+u^2}} \int_{-\infty}^{+\infty} e^{-(\alpha_{34}+\frac{\alpha_{12}u^2}{\alpha_{12}+u^2})(x_2-A_x)^2} dx_2 \\
&= \frac{\pi}{\sqrt{\alpha_{12}\alpha_{34}+\alpha_{1234}u^2}}
\end{aligned}$$

$$\rho = \frac{\alpha_{12}\alpha_{34}}{\alpha_{1234}},\ t^2 = \frac{u^2}{u^2+\rho},\ u^2 = \frac{\rho t^2}{1-t^2},\ du = \frac{\sqrt{\rho}}{(1-t^2)^{3/2}}dt$$

$$\tilde{I}_x(0,0,0,0;t) = \frac{\pi}{\sqrt{\alpha_{12}\alpha_{34}+\alpha_{1234}u^2}} = \frac{\pi\sqrt{1-t^2}}{\sqrt{\alpha_{12}\alpha_{34}}}$$

$$\tilde{I}_x(l_1+l_2,0,l_3+l_4,0;t) = \iint {x_1}_A^{l_1+l_2}{x_2}_A^{l_3+l_4}e^{-\alpha_{12}{x_1}_A^2}e^{-\alpha_{34}{x_2}_A^2}e^{-\frac{\rho t^2}{1-t^2}(x_1-x_2)^2}dx_1dx_2$$

$$\begin{aligned}I_x(l_1+l_2,0,l_3+l_4,0;t) &= \frac{\tilde{I}_x(l_1+l_2,0,l_3+l_4,0;t)}{\tilde{I}_x(0,0,0,0;t)}\\ &= \frac{\iint {x_1}_A^{l_1+l_2}{x_2}_A^{l_3+l_4}e^{-\alpha_{12}{x_1}_A^2}e^{-\alpha_{34}{x_2}_A^2}e^{-\frac{\rho t^2}{1-t^2}(x_1-x_2)^2}dx_1dx_2}{e^{-Xt^2}\frac{\pi\sqrt{1-t^2}}{\sqrt{\alpha_{12}\alpha_{34}}}}\end{aligned}$$

$$X=0,\ e^{-Xt^2}=1$$

$$\begin{aligned}\langle\phi_j\phi_p|\phi_q\phi_k\rangle &= \frac{2}{\sqrt{\pi}}\int_0^\infty \tilde{I}_x(l_1+l_2,0,l_3+l_4,0;u)\tilde{I}_y(m_1+m_2,0,m_3+m_4,0;u)\tilde{I}_z(n_1+n_2,0,n_3+n_4,0;u)du\\ &= \frac{2\pi^{5/2}}{\alpha_{12}\alpha_{34}\sqrt{\alpha_{1234}}}\int_0^1 e^{-Xt^2}I_x(l_1+l_2,0,l_3+l_4,0;t)I_y(m_1+m_2,0,m_3+m_4,0;t)I_z(n_1+n_2,0,n_3+n_4,0;t)dt\\ &= \frac{2\pi^{5/2}}{\alpha_{12}\alpha_{34}\sqrt{\alpha_{1234}}}\sum_{p=1}^{N_p}\omega_p I_x(t_p)I_y(t_p)I_z(t_p)\end{aligned}$$

only need VRR here:
$I_x(l_1+1,0,l_2,0;t) = \frac{l_1}{2\alpha_{12}}(1-\frac{\alpha_{34}t^2}{\alpha_{1234}})I_x(l_1-1,0,l_2,0;t) + \frac{l_2t^2}{2\alpha_{1234}}I_x(l_1,0,l_2-1,0;t)$
$I_x(l_1,0,l_2+1,0;t) = \frac{l_2}{2\alpha_{34}}(1-\frac{\alpha_{12}t^2}{\alpha_{1234}})I_x(l_1,0,l_2-1,0;t) + \frac{l_1t^2}{2\alpha_{1234}}I_x(l_1-1,0,l_2,0;t)$