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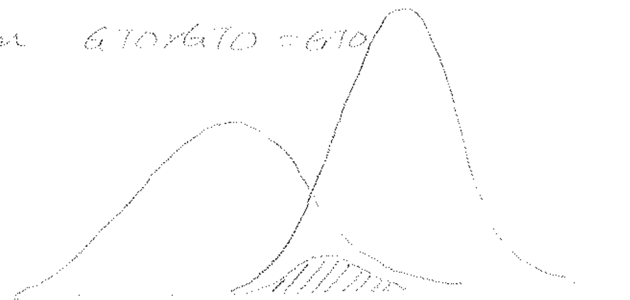
⑥ Gaussian basis set — Boys, Pople, Dunning

(See Project #2 introductory materials first)

$$\chi_\mu(\mathbf{r}) = N_{nlm}\, e^{-\zeta_n r}\, Y_{lm}$$
or
$$= N'_{nlm}\,(x-x_0)^{n_x}(y-y_0)^{n_y}(z-z_0)^{n_z}\, e^{-\zeta|\mathbf{r}-\mathbf{r}_0|}$$
Slater type (STO)

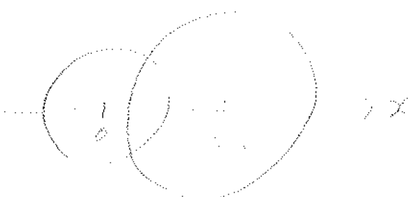
$$\chi_\mu(\mathbf{r}) = N_{nlm}\, e^{-\zeta_n r^2}\, Y_{lm}$$
or
$$= N'_{nlm}\,(x-x_0)^{n_x}(y-y_0)^{n_y}(z-z_0)^{n_z}\, e^{-\zeta|\mathbf{r}-\mathbf{r}_0|^2}$$
Gauss type (GTO)

a) Gaussian Product Theorem GTO×GTO = GTO
b) 3D GTO = (1D GTO)^3
c) Coulomb = $\int$ GTO
d) $-\frac{1}{2}\nabla^2$ GTO = GTO
e) p.d.f GTO = $\frac{\partial^n}{\partial x^n}$ GTO



i) Overlap

$$s_1 = e^{-a(x^2+y^2+z^2)}$$
$$s_2 = e^{-b((x-x_0)^2+(y-y_0)^2+(z-z_0)^2)}$$



$$\left[\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}\right]$$

$$\langle s_1|s_2\rangle = \langle s_1|s_2\rangle_x\, \langle s_1|s_2\rangle_y\, \langle s_1|s_2\rangle_z$$

$$\int_{-\infty}^{+\infty} e^{-ax^2}\, e^{-b(x-x_0)^2}\,dx$$
$$= \int_{-\infty}^{+\infty} e^{-(a+b)\left(x-\frac{bx_0}{a+b}\right)^2 - \frac{abx_0^2}{a+b}}\,dx$$
$$= e^{-\frac{abx_0^2}{a+b}}\sqrt{\frac{\pi}{a+b}}$$

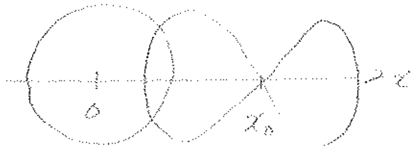
$$e^{-\frac{aby_0^2}{a+b}}\sqrt{\frac{\pi}{a+b}} \qquad e^{-\frac{abz_0^2}{a+b}}\sqrt{\frac{\pi}{a+b}}$$

$$\langle s_1|s_2\rangle = \left(\frac{\pi}{a+b}\right)^{3/2} e^{-\frac{ab(x_0^2+y_0^2+z_0^2)}{a+b}}$$

$$S_1 = e^{-a(x^2+y^2+z^2)}$$

$$P_2 = (x-x_0)\, e^{-b((x-x_0)^2+(y-y_0)^2+(z-z_0)^2)}$$

$$\left(\text{cf. } S_2 = e^{-b((x-x_0)^2+(y-y_0)^2+(z-z_0)^2)}\right)$$



Since x always appears as $(x-x_0)$

$$\frac{\partial}{\partial x} S_2 = -\frac{\partial}{\partial x_0} S_2$$

$$= -2b(x-x_0) S_2$$

note $\frac{\partial}{\partial x_0} S_1 = 0$

$$= -2b\, P_2$$

$$\langle S_1 | P_2 \rangle = \langle S_1 | \frac{1}{2b} \frac{\partial}{\partial x_0} S_2 \rangle = \frac{1}{2b} \frac{\partial}{\partial x_0} \langle S_1 | S_2 \rangle \quad *$$

$$= \frac{1}{2b} \frac{\partial}{\partial x_0} \left(\frac{\pi}{a+b}\right)^{3/2} e^{-\frac{ab}{a+b}(x_0^2+y_0^2+z_0^2)}$$

$$= \frac{1}{2b} \frac{-ab\,2x_0}{a+b} \langle S_1 | S_2 \rangle = \frac{-a x_0}{a+b} \langle S_1 | S_2 \rangle$$

ii) Kinetic

$$S_1 = e^{-a(x^2+y^2+z^2)}$$

$$S_2 = e^{-b((x-x_0)^2+(y-y_0)^2+(z-z_0)^2)}$$

$$\frac{\partial}{\partial x} S_2 = -\frac{\partial}{\partial x_0} S_2$$

$$\frac{\partial^2}{\partial x^2} S_2 = \frac{\partial^2}{\partial x_0^2} S_2$$

$$\langle S_1 | -\frac{1}{2}\nabla^2 | S_2 \rangle = -\frac{1}{2} \langle S_1 | \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} | S_2 \rangle$$

$$= -\frac{1}{2}\left(\frac{\partial^2}{\partial x_0^2} + \frac{\partial^2}{\partial y_0^2} + \frac{\partial^2}{\partial z_0^2}\right) \langle S_1 | S_2 \rangle \quad *$$

$$= -\frac{1}{2}\left(\frac{\partial^2}{\partial x_0^2} + \frac{\partial^2}{\partial y_0^2} + \frac{\partial^2}{\partial z_0^2}\right) \left(\frac{\pi}{a+b}\right)^{3/2} e^{-\frac{ab}{a+b}(x_0^2+y_0^2+z_0^2)}$$

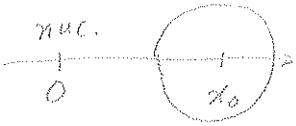
$$\boxed{\begin{aligned} \frac{\partial}{\partial x_0} e^{-\frac{ab}{a+b}x_0^2} &= -\frac{2abx_0}{a+b} e^{-\frac{ab}{a+b}x_0^2} \\ \frac{\partial^2}{\partial x_0^2} e^{-\frac{ab}{a+b}x_0^2} &= -\frac{2ab}{a+b} + 4\left(\frac{ab}{a+b}\right)^2 x_0^2 \end{aligned}}$$

$$= \left(\frac{3ab}{a+b} - 2\left(\frac{ab}{a+b}\right)^2 (x_0^2+y_0^2+z_0^2)\right) \langle S_1 | S_2 \rangle$$

iii) Nuclear attraction

$$s_1 = e^{-b((x-x_0)^2+y^2+z^2)}$$

$$s_2 = e^{-b((x-x_0)^2+y^2+z^2)}$$



$$\frac{1}{r} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty} e^{-r^2u^2}\,du \qquad r = (x^2+y^2+z^2)^{1/2}$$

$$\langle s_1 | \frac{1}{r} | s_2 \rangle = \int_{-\infty}^{+\infty} \frac{e^{-2b(x-x_0)^2-2by^2-2bz^2}}{r}\,dx\,dy\,dz$$

$$= \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-2b(x-x_0)^2-2by^2-2bz^2-r^2u^2}\,dx\,dy\,dz\,du$$

$r^2 \rightarrow x^2+y^2+z^2$

$$= \frac{1}{\sqrt{\pi}}\int\left(\int e^{-2b(x-x_0)^2-x^2u^2}dx \int e^{-2by^2-y^2u^2}dy \int e^{-2bz^2-z^2u^2}dz\right)du$$

$$\int e^{-(2b+u^2)\left(x-\frac{2bx_0}{2b+u^2}\right)^2-\frac{2bu^2}{2b+u^2}x_0^2}\,dx$$

$$= \sqrt{\frac{\pi}{2b+u^2}}\; e^{-\underbrace{\frac{2bu^2}{2b+u^2}}_{=t^2}x_0^2}$$

$$\sqrt{\frac{\pi}{2b+u^2}}$$

$$t^2 = \frac{u^2}{2b+u^2} \qquad \begin{array}{ll} u & -\infty \rightarrow 0 \rightarrow \infty \\ t & 1 \rightarrow 0 \rightarrow 1 \end{array}$$

$$2\frac{dt}{du}\cdot t = \frac{4bu}{(2b+u^2)^2}$$

$$du = \frac{(2b+u^2)^2}{2bu}\frac{u}{\sqrt{2b+u^2}}\,dt = \frac{(2b+u^2)^{3/2}}{2b}\,dt$$

$$= \pi\int_{-\infty}^{+\infty}\frac{1}{(2b+u^2)^{3/2}}\,e^{-\frac{2bx_0^2u^2}{2b+u^2}}\,du$$

$$= 2\pi\int_0^1 \frac{1}{2b}\,e^{-2bx_0^2t^2}\,dt$$

$$= 2\left(\frac{\pi}{2b}\right)F_0(2bx_0^2)$$

$$= 2\left(\frac{2b}{\pi}\right)^{1/2}\langle s_1|s_2\rangle F_0(2bx_0^2)$$

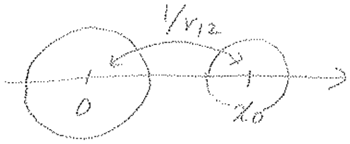
$$\boxed{F_m(T) = \int_0^1 t^{2m}e^{-Tt^2}\,dt}$$

FMT

iv) Electron repulsion integrals (ERI)

$$s_1 = e^{-a(x_1^2+y_1^2+z_1^2)} \qquad s_3 = e^{-a((x_2-x_0)^2+y_2^2+z_2^2)}$$

$$s_2 = e^{-a(x_1^2+y_1^2+z_1^2)} \qquad s_4 = e^{-a((x_2-x_0)^2+y_2^2+z_2^2)}$$



$$\frac{1}{r_{12}} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty} e^{-r_{12}^2 u^2}\,du \qquad r_{12} = \left((x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2\right)^{1/2}$$

$$(s_1 s_2 | \tfrac{1}{r_{12}} | s_3 s_4) = \iint \frac{e^{-2a(x_1^2+y_1^2+z_1^2)}\, e^{-2a((x_2-x_0)^2+y_2^2+z_2^2)}}{r_{12}}\, dx_1 dy_1 dz_1\, dx_2 dy_2 dz_2$$

$$\begin{aligned}
e^{-2ay_1^2-2ay_2^2-(y_1-y_2)^2u^2} &= e^{-(2a+u^2)y_1^2-(2a+u^2)y_2^2+2y_1y_2u^2} \\
&= e^{-(2a+u^2)\left(y_1-\frac{y_2u^2}{2a+u^2}\right)^2+\frac{y_2^2u^4}{2a+u^2}-(2a+u^2)y_2^2} \\
&= \underbrace{e^{-(2a+u^2)\left(y_1-\frac{y_2u^2}{2a+u^2}\right)^2}}_{\int dy_1 \;\to\; \sqrt{\frac{\pi}{2a+u^2}}}\; e^{\underbrace{-\left(2a+u^2-\frac{u^4}{2a+u^2}\right)}_{-\frac{4a^2+4au^2}{2a+u^2}} y_2^2}
\end{aligned}$$

$$\int dy_2 \;\to\; \sqrt{\frac{\pi(2a+u^2)}{4a(a+u^2)}}$$

$$\begin{aligned}
e^{-2ax_1^2-2a(x_2-x_0)^2-(x_1-x_2)^2u^2} &= e^{-(2a+u^2)x_1^2-(2a+u^2)x_2^2+4ax_2x_0+2x_2x_1u^2-2ax_0^2} \\
&= \underbrace{e^{-(2a+u^2)\left(x_1-\frac{x_2u^2}{2a+u^2}\right)^2}}_{\int dx_1 \;\to\; \sqrt{\frac{\pi}{2a+u^2}}}\; e^{\underbrace{\frac{x_2^2u^4}{2a+u^2}-(2a+u^2)x_2^2}_{-\frac{4a^2+4au^2}{2a+u^2}x_2^2}+4ax_2x_0-2ax_0^2}
\end{aligned}$$

$$-\frac{4a^2+4au^2}{2a+u^2}\left(x_2-\frac{(2a+u^2)x_0}{2a+2u^2}\right)^2-\frac{au^2}{a+u^2}x_0^2$$

$$\int dx_2 \;\to\; \sqrt{\frac{\pi(2a+u^2)}{4a(a+u^2)}}\; \underbrace{e^{-\underbrace{\frac{au^2}{a+u^2}}_{t^2}x_0^2}}_{e^{-ax_0^2t^2}}$$

$$\begin{aligned}
(s_1 s_2|\tfrac{1}{r_{12}}|s_3 s_4) &= \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\left(\frac{\pi}{2a+u^2}\right)^{3/2}\left(\frac{\pi(2a+u^2)}{4a(a+u^2)}\right)^{3/2} e^{-at^2x_0^2}\,du \\
&= \frac{\pi^3}{\sqrt{\pi}}\,\frac{2}{a}\int_0^1\left(\frac{1}{4a}\right)^{3/2} e^{-ax_0^2t^2}\,dt \\
&= 2\left(\frac{a}{\pi}\right)^{1/2}\underbrace{(s_1|s_2)}_{\left(\frac{\pi}{2a}\right)^{3/2}}\underbrace{(s_3|s_4)}_{\left(\frac{\pi}{2a}\right)^{3/2}}\,F_0(ax_0^2)
\end{aligned}$$

$$du = \frac{(a+u^2)^{3/2}}{a}\,dt$$

T. Helgaker, P. Jørgensen, and J. Olsen,
"Molecular Electronic Structure"

A. Szabo and N. S. Ostlund,
"Modern Quantum Chemistry" Appendix

S. Obara and A. Saika, J. Chem. Phys. 84, 3963 (1986)

L. E. McMurchie and E. R. Davidson, J. Comput. Phys. 26, 218 (1978).

M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. 65, 111 (1976).