Ex 1)

Consider two electron and $\sigma_1 = \sigma_2$ (forget spin). Suppose electrons are in Gaussian wave-packets about $x = a$ and $x = -a$

$$\varphi^{\pm}_{\mu}(x) = \frac{\mu}{\sqrt{\pi}} \exp\left(-\mu^2 (x \pm a)^2/2\right).$$

- Build a properly normalised w-f. (use $X_{cm} = \frac{x_1 + x_2}{2}$, $x = x_1 - x_2$)
- Compute the probability density ρ for the separation between the two electrons
- $\langle X_{cm} \rangle = ?$ $\langle x \rangle = ?$ $\langle x^2 \rangle ?$ What happens for $\mu \gg 1$. And for $a \ll 1$?
- Repeat for bosons of spin 0
- Discuss qualitatively the different behaviour ρ

- $\varphi_A(x_1, x_2) = N\left[\varphi^{+}_{\mu}(x_1)\varphi^{-}_{\mu}(x_2) - \varphi^{-}_{\mu}(x_1)\varphi^{+}_{\mu}(x_2)\right]$ N normalisation

$$= N \frac{\mu^2}{\pi} e^{-\mu^2 a^2} e^{-\mu^2 (x_1^2 + x_2^2)/2} \left(e^{-\mu^2 (x_2 - x_1) a} - e^{-\mu^2 (x_1 - x_2) a} \right) = [X_{cm}, x]$$

$$= 2N \frac{\mu^2}{\pi} e^{-\mu^2 a^2} e^{-\mu^2 X_{cm}^2} e^{-\mu^2 x^2/4} \sinh(\mu^2 a x)$$

$$\int |\varphi_A|^2 \, dx \, dX_{cm} \overset{!}{=} 1 = 4N^2 \frac{\mu^4}{\pi^2} e^{-2\mu^2 a^2} \left(\int_{-\infty}^{+\infty} dX_{cm} \, e^{-2\mu^2 X_{cm}^2} \right) \cdot$$

$$\cdot \left(\int_{-\infty}^{+\infty} dx \, e^{-\mu^2 x^2/2} \sinh^2(\mu^2 a x) \right) =$$

$$= 4N^2 \frac{\mu^4}{\pi^2} e^{-2\mu^2 a^2} \cdot \frac{\sqrt{\pi}}{\sqrt{2}\,\mu} \frac{\sqrt{\pi}\,(-1 + e^{2a^2\mu^2})}{\mu\sqrt{2}} = 2N^2 \frac{\mu^2}{\pi} \left(1 - e^{-2\mu^2 a^2}\right)$$

$$\Rightarrow \boxed{N = \frac{\sqrt{\pi}}{\sqrt{2}\,\mu} \frac{1}{\sqrt{1 - e^{-2\mu^2 a^2}}}}$$

- $$\Psi(x, X_{cm}) = \frac{\mu\sqrt{2}}{\sqrt{\pi}} \frac{\exp(-\mu^2 a^2)}{\sqrt{1-\exp(-2\mu^2 a^2)}} e^{-\mu^2 X_{cm}^2} e^{-\mu^2 x^2/4} \sinh(\mu^2 a x)$$

$$\rho(x) = \frac{2\mu^2}{\pi} \frac{\exp(-2\mu^2 a^2)}{1-\exp(-2\mu^2 a^2)} \left(\int_{-\infty}^{+\infty} e^{-2\mu^2 X_{cm}^2} dX_{cm}\right) \cdot e^{-\mu^2 x^2/2} \sinh^2(\mu^2 a x) =$$

$$= \frac{\sqrt{2}\mu}{\sqrt{\pi}} \frac{\exp(-2\mu^2 a^2)}{1-\exp(-2\mu^2 a^2)} e^{-\mu^2 x^2/2} \sinh^2(\mu^2 a x)$$

- $\langle X_{cm} \rangle = 0$ by symmetry $\langle x \rangle = 0$ ...

$\langle x^2 \rangle =$ (shift integrals, differentiate under the integral)

$$= \frac{\cancel{\sqrt{2}\mu}}{\cancel{\sqrt{\pi}}} \frac{\exp(-2\mu^2 a^2)}{1-\exp(\cdot\cdot)} \frac{\cancel{\sqrt{\pi}}}{\mu^{3/2}} \frac{1}{\cancel{\sqrt{2}}} \left((1+4a^2\mu^2) e^{2a^2\mu^2} - 1\right)$$

$$= \frac{1}{\mu^2} \frac{1+4\mu^2 a^2 - \exp(-2\mu^2 a^2)}{1-\exp(-2\mu^2 a^2)} \underset{\mu\to\infty}{\sim} 4a^2$$

for $a \to 0$ $\quad \frac{1}{\mu^2} \frac{6\mu^2 a^2}{2\mu^2 a^2} \sim \frac{3}{\mu^2} > 0$

- $\varphi_s(x_1, x_2) = N\left[\varphi_\mu^+(x_1)\varphi_\mu^-(x_2) + \varphi_\mu^-(x_1)\varphi_\mu^+(x_1)\right]$ N normalisation

$$= 2N\frac{\mu^2}{\pi} e^{-\mu^2 a^2} e^{-\mu^2 X_{CM}} e^{-\mu^2 x^2/4} \cosh(\mu^2 x a)$$

$$1 = 4N^2 \frac{\mu^4}{\pi^2} e^{-2\mu^2 a^2} \frac{\sqrt{\pi}}{\sqrt{2}\mu} \int_{-\infty}^{+\infty} dx\, e^{-\mu^2 x^2/2} \left(1 + \sinh^2(\mu^2 a x)\right) =$$

$$\cancel{4}^{2} N^2 \frac{\mu^{\cancel{4}2}}{\pi^{\cancel{2}}} e^{-2\mu^2 a^2} \cancel{\frac{\sqrt{\pi}}{\sqrt{2}\mu}} \cancel{\frac{\sqrt{\pi}}{\sqrt{2}}} \cancel{\frac{1}{\mu}} \left(1 + e^{2a^2\mu^2}\right) = 2N^2 \frac{\mu^2}{\pi} \left(1 + e^{-2a^2\mu^2}\right)$$

$$\Rightarrow \boxed{N = \frac{\sqrt{\pi}}{\sqrt{2}\mu} \frac{1}{\sqrt{1 + e^{-2a^2\mu^2}}}}$$

- $$\psi(x, X_{cm}) = \frac{\mu\sqrt{2}}{\sqrt{\pi}} \frac{\exp(-\mu^2 a^2)}{\sqrt{1 + \exp(-2\mu^2 a^2)}} e^{-\mu^2 X_{cm}^2} e^{-\mu^2 x^2/4} \cosh(\mu^2 a x)$$

$$\boxed{\rho(x) = \frac{\sqrt{2}\mu}{\sqrt{\pi}} \frac{\exp(-2\mu^2 a^2)}{1 + \exp(-2\mu^2 a^2)} e^{-\mu^2 x^2/2} \cosh^2(\mu^2 a x)}$$

- $\langle x \rangle = \langle X_{cm} \rangle = 0$ by symmetry

$$\langle x^2 \rangle = \frac{\sqrt{2}\mu}{\sqrt{\pi}} \frac{\exp(-2\mu^2 a^2)}{1 + \exp(-\cdots)} \frac{\sqrt{\pi}}{\sqrt{2}\mu^3} \left(-1 + e^{+2a^2\mu^2}(1 + 4a^2\mu^2)\right) =$$

$$\boxed{= \frac{1}{\mu^2} \frac{1 + 4a^2\mu^2 - \exp(-2a^2\mu^2)}{1 + \exp(-2a^2\mu^2)}}$$

$\mu \to \infty \quad \sim 4a^2$

$a \to 0 \quad \sim 3a^2 \to 0$

• $\rho_A(x)$ always vanish in $x=0$.

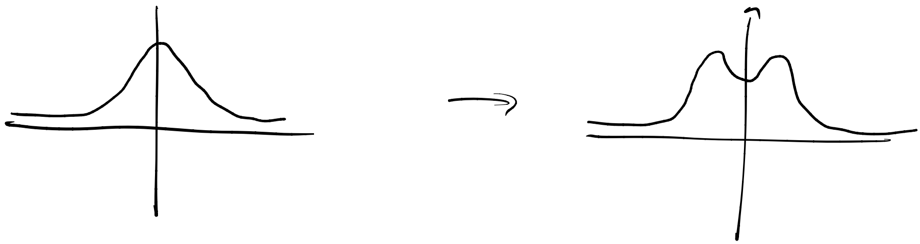
$\rho_S(x)$ does not vanish for $x \to 0$.

The function $f(x) = e^{-x^2/2} \cosh^2(Kx)$

has extrema: $0 = -x \exp(-x^2/2)\cosh^2(Kx) + K\exp(-x^2/2)\, 2\cosh(Kx)\sinh(Kx)$

$$-x\cosh(Kx) + 2K\sinh(Kx) = 0 \Rightarrow \tanh(Kx) = \frac{x}{2K}$$

which has solution $x=0$ and two more if K is sufficiently big.



$K = a\mu$ K big means either big a or large μ or both

very separated

vero

Ex Helium

$$\phi(\vec{r}) = R_{nl}(r)\, Y_{lm}(\theta,\varphi)$$

$$P_l^{(0)}(u) = (-1)^l \frac{1}{2^l l!}\left(\frac{d}{du}\right)^l (1-u^2)^l$$

$$\int_{-1}^{+1} du\, P_l^{(0)}(u)\, P_k^{(0)}(u) = \delta_{kl}\cdot\frac{2}{2l+1}$$

In general

$$Y_{lm}(\theta,\varphi) = \overset{\nearrow \text{norm}}{C_{l,m}}\, e^{im\phi}\frac{1}{\sin^m\theta} P_l^m(\cos\theta)$$

For $m=0$

$$Y_{l0}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}}\, P_l^{(0)}(\cos\theta)$$

$$\int_0^{2\pi} d\varphi \int_{-1}^{+1} d\cos\theta\; Y_{l'}^{m'*}\, Y_l^m = \delta_{ll'}\,\delta_{mm'}$$

Radial functions

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Z\cdot r}{2a_0}\right)e^{-Z\cdot r/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Z\cdot r}{a_0}\, e^{-Z\cdot r/2\cdot a_0}$$

Sph. harm.

$$Y_{00}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\Delta E_1 = J \pm K \qquad \pm \rightarrow \begin{matrix}\text{singlet}\\ \text{triplet}\end{matrix}$$

$$J_l = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2\, \frac{|\phi_{100}(\vec{r}_1)|^2\,|\phi_{2l0}(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}$$

$$K_l = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2\, \frac{\phi_{100}^*(\vec{r}_1)\,\phi_{100}(\vec{r}_2)\,\phi_{2l0}^*(\vec{r}_1)\,\phi_{2l0}(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}$$

The following expansion is useful

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}} = \frac{1}{r_1}\sum_{L\geq 0}\left(\frac{r_2}{r_1}\right)^L P_L^{(0)}(\cos\theta) \quad \text{for } r_1 > r_2$$

Also consider $P_l^{(0)}(\hat{r}\cdot\hat{r}') = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_l^{m*}(\theta_1,\varphi_1)\, Y_l^m(\theta_2,\phi_2)$

$$J_\ell = \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|R_{10}(r_1)|^2 |R_{2\ell}(r_2)|^2}{|\vec{r}_1-\vec{r}_2|} \underbrace{\frac{1}{4\pi}}_{|Y_{00}(\theta,\varphi)|^2} \cdot |\underbrace{Y_{\ell 0}(\theta_2,\varphi_2)}_{\text{"}Y_{\ell 0}(\theta_2)\text{"}}|^2 =$$

$$= \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{(4\pi)^2}(2\ell+1)}_{C_\ell} \int d^3 r_1 d^3 r_2 \frac{|R_{10}(r_1)|^2 |R_{2\ell}(r_2)|^2}{|\vec{r}_1-\vec{r}_2|} |P_\ell^{(0)}(\cos\theta_2)|^2 =$$

$$= C_\ell \cdot \int_0^{+\infty} dr_1\, r_1^2 |R_{10}(r_1)|^2 \int_0^{+\infty} dr_2\, r_2^2 |R_{2\ell}(r_2)|^2 \int d\Omega_1 d\Omega_2 \frac{|P_\ell^{(0)}(\cos\theta_2)|^2}{|\vec{r}_1-\vec{r}_2|} =$$

$$= C_\ell \int_0^{+\infty} dr_1\, r_1^2 |R_{10}(r_1)|^2 \Bigg[\Bigg(\int_0^{r_1} dr_2\, r_2^2 |R_{2\ell}(r_2)|^2 \frac{1}{r_1}\sum_{L\geq 0}\left(\frac{r_2}{r_1}\right)^L \int d\Omega_1 d\Omega_2\, P_L^{(0)}(\cos\theta_{12})$$

$$\cdot |P_\ell^{(0)}(\cos\theta_2)|^2\Bigg) + \Bigg(\int_{r_1}^{+\infty} dr_2\, r_2^2 |R_{2\ell}(r_2)|^2 \frac{1}{r_2}\sum_{L\geq 0}\left(\frac{r_1}{r_2}\right)^L \int d\Omega_1 d\Omega_2\, P_L^{(0)}(\cos\theta_{12}) \cdot$$

$$\cdot |P_\ell^{(0)}(\cos\theta_2)|^2\Bigg)\Bigg] = \star$$

what is it: $\int d\Omega_1 d\Omega_2\, P_L^{(0)}(\cos\theta_{12}) |P_\ell^{(0)}(\cos\theta_2)|^2 =$ ↳ Rotate Ω_1

$$= \delta_{L0} \cdot 4\pi \int d\Omega_2 |P_\ell^{(0)}(\cos\theta_2)|^2 = \delta_{L0} \cdot \frac{16\pi^2}{2\ell+1}$$

$$\star\ C_\ell \frac{16\pi^2}{2\ell+1} \int_0^\infty dr_1\, r_1^2 |R_{10}(r_1)|^2 \left[\int_0^{r_1} dr_2 \frac{r_2^2}{r_1} |R_{2\ell}(r_2)|^2 + \right.$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2 |R_{2\ell}(r_2)|^2 \right] =$$

$$= \frac{e^2}{4\pi\varepsilon_0} \int_0^\infty dr_1\, r_1^2 |R_{10}(r_1)|^2 \left[\int_0^{r_1} dr_2 \frac{r_2^2}{r_1}|R_{2\ell}(r_2)|^2 + \int_{r_1}^{+\infty} dr_2\, r_2 |R_{2\ell}(r_2)|^2\right]$$

$$J_0 = \frac{e^2}{4\pi\varepsilon_0} \cdot 2\left(\frac{Z}{a_0}\right)^6 \cdot$$

$$\cdot \int_0^{+\infty} dr_1\, r_1^2\, e^{-\frac{2Z\cdot r}{a_0}} \left[\int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1}\left(1-\frac{Z\cdot r_2}{2a_0}\right) e^{2-\frac{Z\cdot r_2}{a_0}} + \right.$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2 \left(1-\frac{Z\cdot r_2}{2a_0}\right)^2 e^{-\frac{Z r_2}{a_0}} \right] = \text{(Mathematica)}$$

$$= \boxed{\frac{e^2}{4\pi\varepsilon_0}\,\frac{17}{81}\,\frac{Z}{a_0}}$$

$$J_1 = \frac{e^2}{4\pi\varepsilon_0}\,\frac{1}{8}\,\frac{4}{3}\left(\frac{Z}{a_0}\right)^6 \cdot$$

$$\cdot \int_0^{+\infty} dr_1\, r_1^2\, e^{-\frac{2Z\cdot r}{a_0}} \left[\int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1}\left(\frac{Z\cdot r_2}{a_0}\right)^2 e^{-\frac{Z r_3}{a_0}} + \right.$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2 \left(\frac{Z\cdot r_2}{a_0}\right)^2 e^{-\frac{Z r_3}{a_0}} \right] = \boxed{\frac{e^2}{4\pi\varepsilon_0}\,\frac{59}{243}\,\frac{Z}{a_0}}$$

$$K_\ell = \frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2\, \frac{1}{|\vec{r}_1-\vec{r}_2|}\,\frac{1}{4\pi}\, R_{10}(r_1)R_{10}(r_2)\cdot R_{2\ell}(r_1)\, R_{2\ell}(r_2)$$

$$\cdot\, Y_{\ell 0}(\theta_1,\varphi_1)\, Y_{\ell 0}(\theta_2,\varphi_2) = \underbrace{\frac{e^2}{4\pi\varepsilon_0}\,\frac{2\ell+1}{(4\pi)^2}}_{C_\ell}\int d^3r_1\, d^3r_2\, \frac{RRRR}{|\vec{r}_1-\vec{r}_2|}\, P_\ell^{(0)}(\cos\theta_1)P_\ell^{(0)}(\cos\theta_2)$$

$$= C_\ell\int_0^{+\infty} dr_1\, r_1^2\, \underbrace{R_{10}(r_1)R_{2\ell}(r_1)}_{f_\ell(r_1)}\int_0^{+\infty} dr_2\, r_2^2\, \underbrace{R_{10}(r_2)R_{2\ell}(r_2)}_{f_\ell(r_2)}\int d\Omega_1\, d\Omega_2\, \frac{1}{|\vec{r}_1-\vec{r}_2|}\, P_\ell^{(0)}(\cos\theta_1)P_\ell^{(0)}(\cos\theta_2)$$

$$= C_\ell\int_0^{+\infty} dr_1\, r_1^2 f_\ell(r_1)\sum_{L\geq 0}\left[\int_0^{r_1} dr_2\, r_2^2\,\frac{1}{r_1}\left(\frac{r_2}{r_1}\right)^L \underbrace{\int d\Omega_1\, d\Omega_2\, P_L^{(0)}(\cos\theta_{12})\, P_\ell^{(0)}(\cos\theta_1)\, P_\ell^{(0)}(\cos\theta_2)}_{I_\Omega}\right.$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2^2\,\frac{1}{r_2}\left(\frac{r_1}{r_2}\right)^L \underbrace{\int d\Omega_1\, d\Omega_2\, P_L^{(0)}(\cos\theta_{12})\, P_\ell^{(0)}(\cos\theta_1)\, P_\ell^{(0)}(\cos\theta_2)}_{I_\Omega}\right] = *$$

$$I_\Omega = \frac{4\pi}{2L+1}\,\frac{4\pi}{2\ell+1}\sum_{m=-L}^{+L}\int d\phi_1\, d\cos\theta_1\, d\phi_2\, d\cos\theta_2\, Y_L^{m*}(\theta_1,\varphi_1)\, Y_L^{m}(\theta_2,\varphi_2)\, Y_\ell^{(0)}(\theta_1,\varphi_1)\, Y_\ell^{(0)*}(\theta_2,\varphi_2)$$

$$= \delta_{L\ell}\,\frac{(4\pi)^2}{(2\ell+1)^2}$$

$$* \; C_\ell\,\frac{(4\pi)^2}{(2\ell+1)^2}\int_0^{+\infty} dr_1\, r_1^2 f_\ell(r_1)\left[\int_0^{r_1} dr_2\, r_2^2\,\frac{1}{r_1}\left(\frac{r_2}{r_1}\right)^\ell f_\ell + \int_{r_1}^{+\infty} dr_2\, r_2\left(\frac{r_1}{r_2}\right)^\ell f_\ell\right] =$$

$$= \frac{e^2}{4\pi\varepsilon_0}\,\frac{1}{2\ell+1}\cdot\int_0^{+\infty} dr_1\, r_1^2\, R_{10}(r_1)R_{2\ell}(r_1)\,\cdot$$

$$\cdot\left[\int_0^{r_1} dr_2\, r_2^2\,\frac{1}{r_1}\left(\frac{r_2}{r_1}\right)^\ell R_{10}(r_2)R_{2\ell}(r_2) + \int_{r_1}^{+\infty} dr_2\, r_2\left(\frac{r_1}{r_2}\right)^\ell R_{10}(r_2)R_{2\ell}(r_2)\right]$$

$$K_0 = \frac{e^2}{4\pi\varepsilon_0}\frac{16}{8}\left(\frac{Z}{a_0}\right)^6 \cdot \int_0^{+\infty} dr_1\, r_1^2 \left(1-\frac{Zr_1}{2a_0}\right) e^{-\frac{3}{2}\frac{Zr_1}{a_0}} \cdot$$

$$\cdot \left[\int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1}\left(1-\frac{Zr_2}{2a_0}\right) e^{-\frac{3}{2}\frac{Z\cdot r_2}{a_0}} + \right.$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2 \left(1-\frac{Zr_2}{2a_0}\right) e^{-\frac{3}{2}Z\cdot\frac{r_2}{a_0}} \right] = [\text{Mathematica}]$$

$$= \boxed{\frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{a_0}\right)\frac{16}{729}}$$

$$K_1 = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\cdot\frac{4}{8}\frac{1}{3}\left(\frac{Z}{a_0}\right)^6 \cdot \int_0^{r_1} dr_1\, r_1^2 \frac{Zr_1}{a_0} e^{-\frac{3}{2}\frac{Z\cdot r_1}{a_0}} \cdot \left[\right.$$

$$\int_0^{r_1} dr_2\, r_2^2 \frac{1}{r_1}\frac{r_2}{r_1}\frac{Zr_2}{a_0} e^{-\frac{3}{2}\frac{Z\cdot r_2}{a_0}} +$$

$$\left. + \int_{r_1}^{+\infty} dr_2\, r_2^2 \frac{1}{r_2}\frac{r_1}{r_2}\frac{Zr_2}{a_0} e^{-\frac{3}{2}\frac{Z\cdot r_2}{a_0}} \right] = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{12}\left(\frac{Z}{a_0}\right)^8 \cdot$$

$$\cdot \int_0^{r_1} dr_1\, r_1^3 e^{-\frac{Zr_1}{a_0}\frac{3}{2}} \left[\int_0^{r_1} dr_2 \frac{r_2^4}{r_1^2} e^{-\frac{3}{2}\frac{Z\cdot r_2}{a_0}} + \int_{r_1}^{+\infty} dr_2\, r_1 r_2 e^{-\frac{3}{2}\frac{Z\cdot r_2}{a_0}} \right]$$

$$= \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{a_0}\right)\frac{1}{12}\frac{224}{729} = \boxed{\frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{a_0}\right)\frac{56}{2187}}$$