Lecture 10 - Exchange "Forces" 03/03/15

Why don't we have to worry about the second electron?

consider a 2-fermion state

$|\psi\rangle = \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle)$

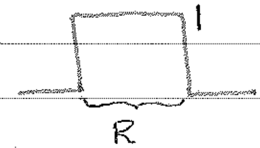
probability to find particle in R:

$\underline{\quad | R | \quad}$

sum of exp. value for each Fermion

$P_R = \langle\psi| P_R^{x_1} + P_R^{x_2} |\psi\rangle$

$\hookrightarrow P_R^x = \begin{cases} 1 & \text{if } x \in R \\ 0 & \text{else} \end{cases} =$



Projection

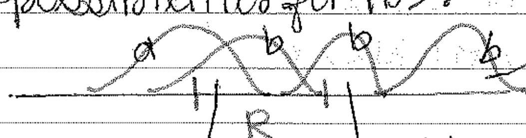
$\langle\psi| P_R^{x_1} |\psi\rangle = \frac{1}{2}(\langle ab| P^{x_1} |ab\rangle + \langle ba| P^{x_2} |ba\rangle - \langle ab| P^{x_1} |ba\rangle - \langle ba| P^{x_2} |ab\rangle)$

$= \frac{1}{2}(\underbrace{\langle a|P|a\rangle}_{\text{projection into state } |a\rangle} + \underbrace{\langle b|P|b\rangle}_{\text{projection into state } |b\rangle} - (\langle a|P|b\rangle \underbrace{\langle b|a\rangle}_{=0 \text{ if } a\&b \text{ are orthog. (\& have no overlap)}} + \text{comp. conj}))$

$\to P_R = \langle a|P|a\rangle + \langle b|P|b\rangle - 2\,\mathrm{Re}\{\langle a|P|b\rangle\langle b|a\rangle\}$

$\uparrow \langle\psi| P_R^{x_2} |\psi\rangle$ gives all same terms

possibilities for $|b\rangle$:



$\langle b|P|b\rangle = 0$ here

$\langle b|a\rangle = 0$ in this case

$\langle b|a\rangle \neq 0$ here due to overlap of $|a\rangle$ & $|b\rangle$

Conclusion: identical particles that are localized outside the region of interest can be ignored (why we don't have to consider every e^- in universe for every calculation)

Q2: What is the [avg.] RMS distance between particles 1&2?

$\langle\psi_\pm|(x_1 - x_2)^2|\psi_\pm\rangle$

from normalization (two factors of $1/\sqrt{2}$)

$\langle\psi_\pm|x_1^2|\psi_\pm\rangle = \frac{1}{2}(\langle ab|x_1^2|ab\rangle + \langle ba|x_1^2|ba\rangle \pm \langle ab|x_1^2|ba\rangle \pm \langle ba|x_1^2|ab\rangle)$

$= \frac{1}{2}(\underbrace{\langle x^2\rangle_a}_{\text{a-exp. val.}} + \underbrace{\langle x^2\rangle_b}_{\text{b-exp. val.}} \pm (\langle a|x^2|b\rangle\langle b|a\rangle + \text{c.c.})$

$-2\langle\psi_\pm|x_1x_2|\psi_\pm\rangle = -\big(\underbrace{\langle ab|x_1x_2|ab\rangle + \langle ba|x_1x_2|ba\rangle}_{2\langle x\rangle_a\langle x\rangle_b} \pm \underbrace{\langle ab|x_1x_2|ba\rangle + c.c.}_{2|\langle a|x|b\rangle|^2}\big)$

$\therefore \langle(x_1-x_2)^2\rangle_\pm = \langle x^2\rangle_a + \langle x^2\rangle_b \pm \langle a|x^2|b\rangle\langle b|a\rangle + c.c.$
$-2\langle x\rangle_a\langle x\rangle_b \mp 2|\langle a|x|b\rangle|^2$

Δx_a^2 variance

$= \underbrace{(\langle x^2\rangle_a - \langle x\rangle_a^2)}_{(\Delta x^2)_a} + \langle x\rangle_a^2 + (\Delta x^2)_b + \langle x\rangle_b^2 - 2\langle x\rangle_a\langle x\rangle_b$

$(\langle x\rangle_a - \langle x\rangle_b)^2$

$\mp \underbrace{2|\langle a|x|b\rangle|^2}_{\geq 0} \pm (\langle a|x^2|b\rangle\langle b|a\rangle + c.c.)$

≥ 0, this term will always increase the avg. distance between particles for neg. wfn.

fermionic case (where + is bosonic case)

For $|\psi_-\rangle = \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle)$

if $|b\rangle$ is partially orthogonal

$|b\rangle = \underbrace{c_1|a\rangle}\, + c_2|a_\perp\rangle$

this term would cancel out for the negative wfn state (non orthog. piece drops out of anti-symmetric expression)

Exchange Interaction

For the He atom

consider the states: $\frac{1}{2}(|1s\rangle|2l\rangle \pm |2l\rangle|1s\rangle)(|+-\rangle \mp |-+\rangle) = |\pm\rangle$

- consider the effects of interaction:

What is the effect on the energy of

$\mathcal{H}_{int} = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$?

inter. hamil, a scalar op

$\rightarrow \mathcal{H}_{int}$ already diagonal in degen subspc., so we can just compute the expectation val.

$\langle\pm|\mathcal{H}_{int}|\pm\rangle = \frac{1}{2}\langle 1s, 2l|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}|1s, 2l\rangle + \ldots$

$$= \int d^3r_1 d^3r_2 \, |\psi_{1S}(\vec{r}_1)|^2 \, |\psi_{2S}(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

this is the natural exp. for the exp. val, but it leaves out the inter/cross-terms

actually = " " $\pm \underbrace{\mathrm{Re}\left(\langle 1S, 2S | \frac{e^2}{|r_1 - r_2|} | 2S, 1S \rangle \right)}_{\text{exchange integral or interaction}}$

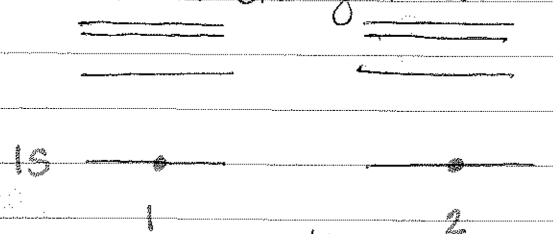
+ → symmetrized wfn enhanced inter.

− → anti-symm.

How close can we get for He w/ Variational Principle

Non-interacting He levels

He levels



singlet spin-state

$$E_n = \frac{-Z^2}{n^2} \underset{\text{Rydberg const.}}{Ry} = \frac{-4}{n^2} Ry$$

$\rightarrow E_0^{(0)} = -8\,Ry$

what about $\mathcal{H}_{int} = e^2/|\vec{r}_1 - \vec{r}_2|$?

$\langle 0 | \mathcal{H}_{int} | 0 \rangle = \underbrace{+5/2\,Ry}_{\text{perturbation in } E_0}$

$E_0 = E_0^{(0)} + E_0^{(1)} = -8\,Ry + 5/2\,Ry = -5.5\,Ry$

↳ $E_{0,exp} = -5.8\,Ry$

but we can improve upon this using simple Var. Pr.

Consider: $\frac{1}{\sqrt{\pi}} \left(\frac{Z_*}{a} \right)^{3/2} e^{-Z_* r/a}$

as the variational ansatz.

- vary Z_*, find the minimum $\langle Z^* | \mathcal{H}_{int} | Z^* \rangle$

↳ min @ $Z_* = Z - 5/16$

$E_0 \approx -5.7\,Ry$ for $Z = 2$, He case