

Overlap Term

$$\Sigma_{\text{Caso}}^{R_A} = \sum_{\mu\nu} X_{\mu\nu} S_{\mu\nu}^{R_A} + \text{gauge term} + \text{nuclear term}$$

Energy terms

$$\frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}^{\alpha} (H_{\mu\nu} + F_{\mu\nu}^{\alpha}) +$$

Separated out into α and β

$$\frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}^{\beta} (H_{\mu\nu} + F_{\mu\nu}^{\beta})$$

electron terms \rightarrow Recombine to make things easier

$$\sum P_{\mu\nu}^{\text{tot}} (H_{\mu\nu} + F_{\mu\nu}^{\text{tot}})$$

We care about changes in NUCLEAR position effect on electrons, so only care about forces that affect ~~area~~ depend on position.

Frob terms - only care about

$$F_{\mu\nu} = \frac{1}{2} (\beta_A + \beta_B) S_{\mu\nu} - P_{\mu\nu}^{\alpha} Y_{AB}^{\alpha}$$

$\mu \neq \nu$



overlap itself is

dependent on coordinates

$$\text{so } y = \text{coeff } x^n$$

$$y' = n \text{coeff } x^{n-1}$$

so $\frac{1}{2} (\beta_A + \beta_B)$ is like
one coeff and will be
part of $X_{\mu\nu}$

Same goes for $H_{\mu\nu} = \frac{1}{2} (\beta_A + \beta_B) S_{\mu\nu}$

Same proportionality factor on the

$S_{\mu\nu}$ term

NEED derivation of
 $S_{\mu\nu}$ w/r/t coordinates

From lab slides:

S_{uv}^{lk} is non-zero when

~~$U \in A, V \in B, A \neq B$~~

$V \in A, U \in B, B \neq A$

which basically means
only when the overlap is
calculated on two diff.
atoms is the overlap
non-zero

also given:

$$S_{uv}^{lk} = \sum_{k=1}^3 \sum_{l=1}^3 d_{ku}^{l'} d_{lv}^{l'} \frac{25k^l}{2\pi a} \quad \begin{array}{l} \text{--- 3 bc we have 3 primitives for} \\ \text{each gaussian} \end{array}$$

↑
Coef of the primitives
!! Need to Normalize!!

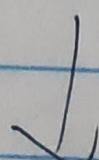
individual primitive overlap

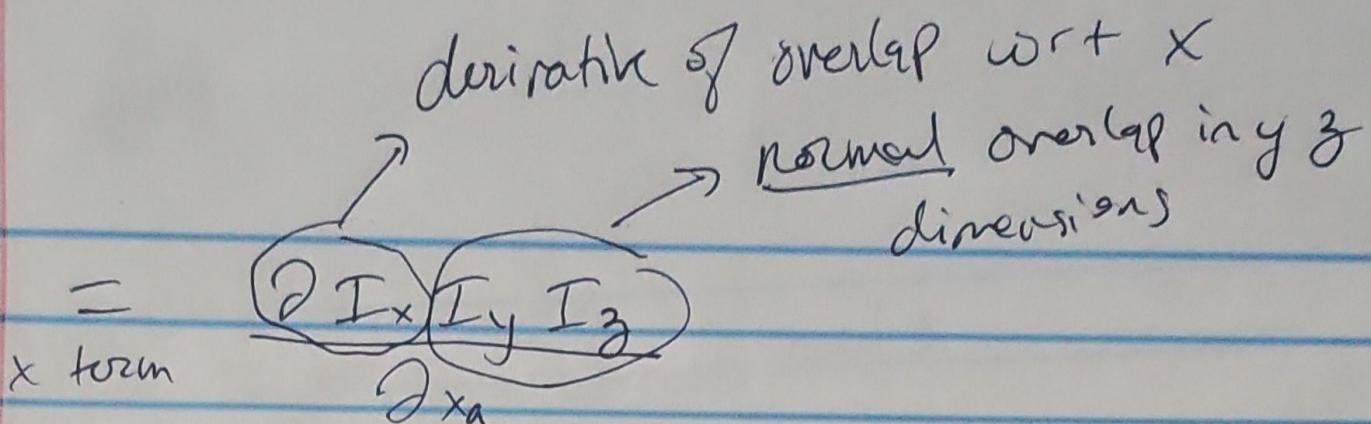
Need

$$\frac{25^k}{2\pi a}$$

→ Separate into xyz components

$$\frac{25^k}{2\pi a} = \frac{25^k}{2\pi a_x}, \frac{25^k}{2\pi a_y}, \frac{25^k}{2\pi a_z}$$





~~$\frac{\partial I_x}{\partial y_a}$~~

y term

$$\frac{I_x \partial I_y I_z}{\partial y_a}$$

z term

$$\frac{I_x I_y \partial I_z}{\partial z_a}$$

So need both the "regular" overlap in each dimension \rightarrow calculated in Hw3?

Still leaves $\frac{\partial I_n}{\partial n_A}$ to solve.

$$\frac{\partial I_x}{\partial x_a} = \frac{\partial}{\partial x_a} \int \text{sum from slides}$$

↓
Simple derivative

$$= -l_A \int dx (x-x_A)^{l_A-1} (x-x_B)^{l_B} e^{-\alpha(x-x_A)^2} e^{-\alpha(x-x_B)^2}$$

$$+ 2\alpha \int dx (x-x_A)^{l_A-1} (x-x_B)^{l_B} e^{-\alpha(x-x_A)^2} e^{-\alpha(x-x_B)^2}$$

~~This is the same integral form as
The overlap!~~

So to get $S_{uv}^{R_a}$ I need:

~~to calculate overlap of~~

for every ~~pair~~ pair of AOs

↳ if on different Atoms

↳ for every pair of primitives

↳ 1D overlap of each dim
then compute again w/ l_a , l_b , $l_a + l_b$

So need to call

inner overlap ($d_A, d_B, x_A, x_B, l_a, l_B$)

$\partial I_x \leftarrow$ - l_a • inner overlap ($d_A, d_B, x_A, x_B, l_a + l_b, l_B$)

+ $2l_a$ inner-overlap ($d_A, d_B, x_A, x_B, l_a - l_b, l_B$)

But then need the other dimensions

bc this give ∂I_x but need to multiply by $\partial I_y \partial I_z$
to get

$$\frac{\partial S''}{\partial x} = \frac{\partial I_x \partial I_y \partial I_z}{\partial x}$$

RECAP

$$\sum x_{uv} S_{uv}^{RA}$$

$$2(\beta_A + \beta_B) \rightarrow \beta$$

Calling $(\beta_A + \beta_B) = \beta$

$$\frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}^2 (H_{\mu\nu} + f_{\mu\nu}) \rightarrow \frac{1}{2} \dots \text{ same for } \beta e^-$$

$$\cancel{2 \times \frac{1}{2} \times \left(\frac{1}{2} (\beta) S_{uv} + \frac{1}{2} (\beta) S_{vu} + \dots \right)}$$

constant
wrt S_{uv}

$$P_{\mu\nu}^{\text{tot}} \left(\frac{1}{2} \beta S_{\mu\nu} + \frac{1}{2} \beta S_{vu} - \dots \right)$$

am I missing a $\frac{1}{2} \beta$? $P_{\mu\nu}^{\text{tot}} (\beta S_{uv}) \rightarrow \text{differentiate w.r.t RA}$

$$P_{\mu\nu}^{\text{tot}} \beta \frac{\partial S_{uv}^{RA}}{\partial RA}$$

$$X_{uv} = P_{\mu\nu}^{\text{tot}} \beta = P_{\mu\nu}^{\text{tot}} (\beta_A - \beta_B)$$

$$\frac{\partial S_{uv}^{RA}}{\partial RA} \rightarrow \text{loops I figured out earlier}$$

for AO-1
for AO-2

if atom-1 \neq atom-2

for prim-u in AO-1

for prim-v in AO-2

$\frac{\partial S_{uv}^{RA}}{\partial RA}$ = for AO-1
for AO-2
if atom-1 ≠ atom-2
for prim-u in AO-1
for prim-v in AO-2

~~get~~ get I_x, I_y, I_z
get coeff ~~du dv~~
get $\partial I_x, \partial I_y, \partial I_z$
— as $-1/a \int$ where $(a-1) +$
 $-2 \alpha \int$ where $(a+1)$