Uniform scaling of electronic coords (DFT-1)

$$\boxed{\bar{r}_i \longrightarrow \alpha\, \bar{r}_i}$$

$\uparrow$ non-zero.

$$\psi(\{\bar{r}_i\}) \longrightarrow \psi_\alpha(\{\bar{r}_i\}) = \alpha^{3N/2}\, \psi(\{\alpha \bar{r}_i\})$$

How?

Let's drop the "{ }":

$$\psi(\bar{r}_i) \rightarrow \psi_\alpha(\bar{r}_i) = \alpha^{3N/2}\, \psi(\alpha \bar{r}_i)$$

Preserve normalization on scaling

$$\therefore \quad 1 = \int |\psi_\alpha(\bar{r}_i)|^2 \cancel{d\bar{r}_i} \prod_{i=1}^{N} d\bar{r}_i$$

Q: Does the expression for ψ_α lead to a normalized ψ_α?

i.e, $$1 \overset{?}{=} \int \left| \alpha^{3N/2}\, \psi(\alpha \bar{r}_i) \right|^2 \prod_{i=1}^{N} d\bar{r}_i$$

$$\overset{?}{=} \alpha^{3N} \int |\psi(\alpha \bar{r}_i)|^2 \prod_{i=1}^{N} d\bar{r}_i$$

$(\alpha \bar{r}_1, \alpha \bar{r}_2, \dots, \alpha \bar{r}_N)$

$d\bar{r}_i = \cancel{d\bar{r}_i}$ $dx_i\, dy_i\, dz_i$

3 of them

$$\overset{?}{=} \int |\psi(\alpha \bar{r}_i)|^2 \prod_{i=1}^{N} d(\alpha \bar{r}_i)$$

let $\bar{r}_i' = \alpha \bar{r}_i$

$$\overset{?}{=} \int |\psi(\bar{r}_i')|^2 \prod_{i=1}^{N} d\bar{r}_i' \quad \checkmark$$

$= 1$ as ψ is normalized.

Uniform Scaling

$$\boxed{\rho_\alpha(\bar{r}) = \alpha^3 \rho(\alpha \bar{r})}$$

$$\rho_\alpha(\bar{r}) = N \int |\psi_\alpha(\bar{r}, \bar{r}_2, \ldots \bar{r}_N)|^2 \prod_{\boxed{i=2}}^{N} d\bar{r}_i$$

$$= N \int |\alpha^{3N/2} \psi(\alpha\bar{r}, \alpha\bar{r}_2, \ldots, \alpha\bar{r}_N)| \prod_{i=2}^{N} d\bar{r}_i$$

Remember to square it!

$\cancel{I} / \cancel{N}$

$$= \alpha^3 N \int |\psi(\alpha\bar{r}, \alpha\bar{r}_2, \ldots, \alpha\bar{r}_N)|^2 \prod_{i=2}^{\cancel{N}} d(\alpha\bar{r}_i)$$

Let $\bar{r}_2' = \alpha \bar{r}_2$

$\bar{r}_3' = \alpha \bar{r}_3$ etc

$$= \alpha^3 N \int |\psi(\alpha\bar{r}, \bar{r}_2', \bar{r}_3', \ldots, \bar{r}_N')|^2 \prod_{i=2}^{N} d\bar{r}_i'$$

$$= \alpha^3 \rho(\alpha\bar{r})$$

Uniform Scaling

$$\langle \psi_\alpha | T | \psi_\alpha \rangle = \alpha^2 \langle \psi | T | \psi \rangle$$

$$\langle \psi_\alpha | V_{ee} | \psi_\alpha \rangle = \alpha \langle \psi | V_{ee} | \psi \rangle$$

$$\langle \psi_\alpha | V_{en}(\bar{R}) | \psi_\alpha \rangle = \alpha \langle \psi | V_{en}(\underline{\alpha \bar{R}}) | \psi \rangle \; *$$

$$\hat{T} = \sum_i -\frac{1}{2}\nabla_i^2 \qquad \hat{V}_{en} = \sum_{i=1}^{N} \frac{Z}{|\bar{r}_i - \bar{R}|}$$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{ij} \frac{1}{r_{ij}}$$

can be generalised to include more nuclei.

* Try these out on one or 2 electron systems.

Consider the $\hat{V}_{ee}$ case:

$$\langle \psi_\alpha | V_{ee} | \psi_\alpha \rangle = \int \psi_\alpha^*(\bar{r}_k) \left(\frac{1}{2}\sum_{ij} \frac{1}{r_{ij}} \right) \psi_\alpha(\bar{r}_k) \prod_{k=1}^{N} d\bar{r}_k$$

$$= \int \alpha^{3N} \psi^*(\alpha \bar{r}_k) \frac{1}{2}\sum_{ij} \frac{1}{r_{ij}} \psi(\alpha \bar{r}_k) \prod d\bar{r}_k$$

$$= \int \psi^*(\underline{\alpha \bar{r}_k}) \frac{1}{2}\sum_{ij} \frac{1}{r_{ij}} \psi(\underline{\alpha \bar{r}_k}) \prod d(\underline{\alpha \bar{r}_k})$$

needs to be $\underline{\alpha r_{ij}}$

$$r_{ij} = |\bar{r}_i - \bar{r}_j| = \frac{1}{\alpha} |\alpha \bar{r}_i - \alpha \bar{r}_j|$$

$$= \alpha \int \psi^*(\alpha \bar{r}_k) \frac{1}{2} \sum_{ij} \frac{1}{|\alpha \bar{r}_i - \alpha \bar{r}_j|} \psi(\alpha r_k) \prod d(\alpha \bar{r}_k)$$

Now let $\bar{r}_k' = \alpha \bar{r}_k$

$$= \alpha \int \psi^*(\bar{r}_k') \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}'} \psi(\bar{r}_k) \prod d\bar{r}_k' = \alpha \underline{\langle \psi | V_{ee} | \psi \rangle}$$

Uniform Scaling

In DFT we will write quantities in terms of $\rho(\bar{r})$.

$$\therefore \quad T[\rho] \equiv \langle \psi | T | \psi \rangle$$

$$\cancel{J[\rho] + E_{xc}[\rho] \equiv \langle \psi | V_{ee}}$$

The Coulomb part of $\langle \psi | V_{ee} | \psi \rangle$ will be $J[\rho]$ and the exchange part will be $E_x[\rho]$

We will use the scaling relations:

$$T[\rho_\alpha] = \alpha^2 T[\rho]$$

$$J[\rho_\alpha] = \alpha J[\rho]$$

$$E_x[\rho_\alpha] = \alpha E_x[\rho]$$