QUANTUM CHEMISTRY - 3
DENSITY MATRIX APPROACH
by Prof. univ. dr. habil. Mihai V PUTZ

$$\{|n\rangle\}_{n\in\mathbf{N}}$$

$$\hat{1}=\sum_n |n\rangle\langle n|$$

Structura/FUNCTIILE de BAZA (STARI SELECTATE – FUNDAMENTALE/ELEMENTARE)
In spatiul (TUTUROR) starilor
De existenta a nivelurilor
(energetice) de existenta
a electronilor in sisteme
Multielectronice (chimice)
& UNITATEA DE UNIVERS “1”

“Macro” “Micro/nano” “Fundamental/Universal” (“sub-nanoscopic”)

$$\langle \hat{A}\rangle_k=\frac{\langle\varphi_k|\hat{A}|\varphi_k\rangle}{\langle\varphi_k|\varphi_k\rangle}=\frac{\sum_{n,n'}\langle\varphi_k|n'\rangle\langle n'|\hat{A}|n\rangle\langle n|\varphi_k\rangle}{\sum_n\langle\varphi_k|n\rangle\langle n|\varphi_k\rangle}=\frac{\sum_{n,n'}c_{kn}c^*_{kn'}\langle n'|\hat{A}|n\rangle}{\sum_n|c_{kn}|^2}$$

$$|\varphi_k\rangle=\sum_n c_{kn}|n\rangle$$

REPREZENTARE “ORBITALA”
(a electronului) prin “punctele”
Sale de reprezentare fundamentala /n>!

MEDIA OBSERBABILEI “A”= <observabila in stare masurata pe starea “k”>/
pe starea “k”) <starea ne-masurata, libera, “k”>

“ELECTRONII” reprezentati prin functiile lor de BAZA
(=functiile de unda ale electronilor – PHI
se reprezinta prin (ISTORIA DE) functii de unda
“mai” fundamentale)

De ce?
ELECTRONULUI – ca PARTICULA FUNDAMENTALA a materiei
(ne spun Experimentele, si istoria stintelor naturii)
…ii asociem o stare…o functie de unda- PHI(k)!
/n> - functii de unda FUNDAMENTALE pentru starile electronilor
(asa cum ne invata mecanica cuantica)

AVANTAJUL ABORDARII: Toti electronii din sistem se vor reprezenta
(in structura, dinamica, proprietati) PRIN ACELASI SET DE STARI/VETORI/FUNCTII DE baza {/n>}

Reprezentarea MASURARII pe ELECTRONII “k”

$$\langle\hat{A}\rangle=\frac{\sum_k w_k\langle\hat{A}\rangle_k}{\sum_k w_k}$$

Reprezentarea MASURARII pe FUNCTIILE DE BAZA “n”

$$\langle\hat{A}\rangle=\frac{\sum_{n,n'}\langle n|\hat{\rho}|n'\rangle\langle n'|\hat{A}|n\rangle}{\sum_k w_k}$$

Reprezentarea DENSITATII ELECTRONICE (cu toate interacttile inter-electronice incluse)
pe FUNCTIILE DE BAZA “n”

$$\langle n|\hat{\rho}|n'\rangle=\sum_k w_k\frac{c_{kn}c^*_{kn'}}{\sum_n|c_{kn}|^2}$$

= MATRICEA DENSITATE!
(in reprezentarea functiilor electronice)!

$$\hat{\rho}=\sum_{n,n'}|n\rangle\langle n|\hat{\rho}|n'\rangle\langle n'|=\sum_k\frac{w_k}{\sum_n|c_{kn}|^2}\left(\sum_n c_{kn}|n\rangle\right)\left(\sum_{n'}\langle n'|c^*_{kn'}\right)=\sum_k\frac{w_k}{\sum_n|c_{kn}|^2}|\varphi_k\rangle\langle\varphi_k|$$

$$\langle\varphi_k|\hat{\rho}|\varphi_k\rangle=w_k$$

= MATRICEA DENSITATE
(in reprezentarea functiilor electronice)!

CHIMIA
=Fizica (structura si dinamica materiei)
sistemelor multielectronice

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