Energy, density matrices and reduced density matrices in molecular systems: Grand-canonical electron states

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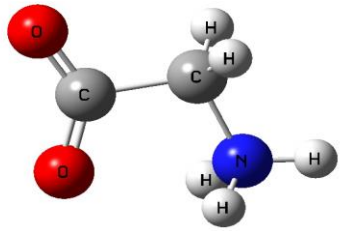
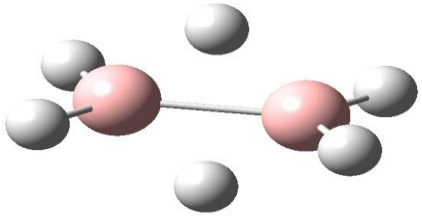
What is a molecule? Views

- Chemical view ≈ set of atoms and bonds



Zwitterionic glycine



Diborane B_2H_6

- Physical view ≈ set of interacting particles: nuclei and electrons

Conciliate both views

Starting point: solving the Schrödinger equation

Many-body problem
(really few)

↓

$$H\Psi = E\Psi$$

To extract the information contained within the state function

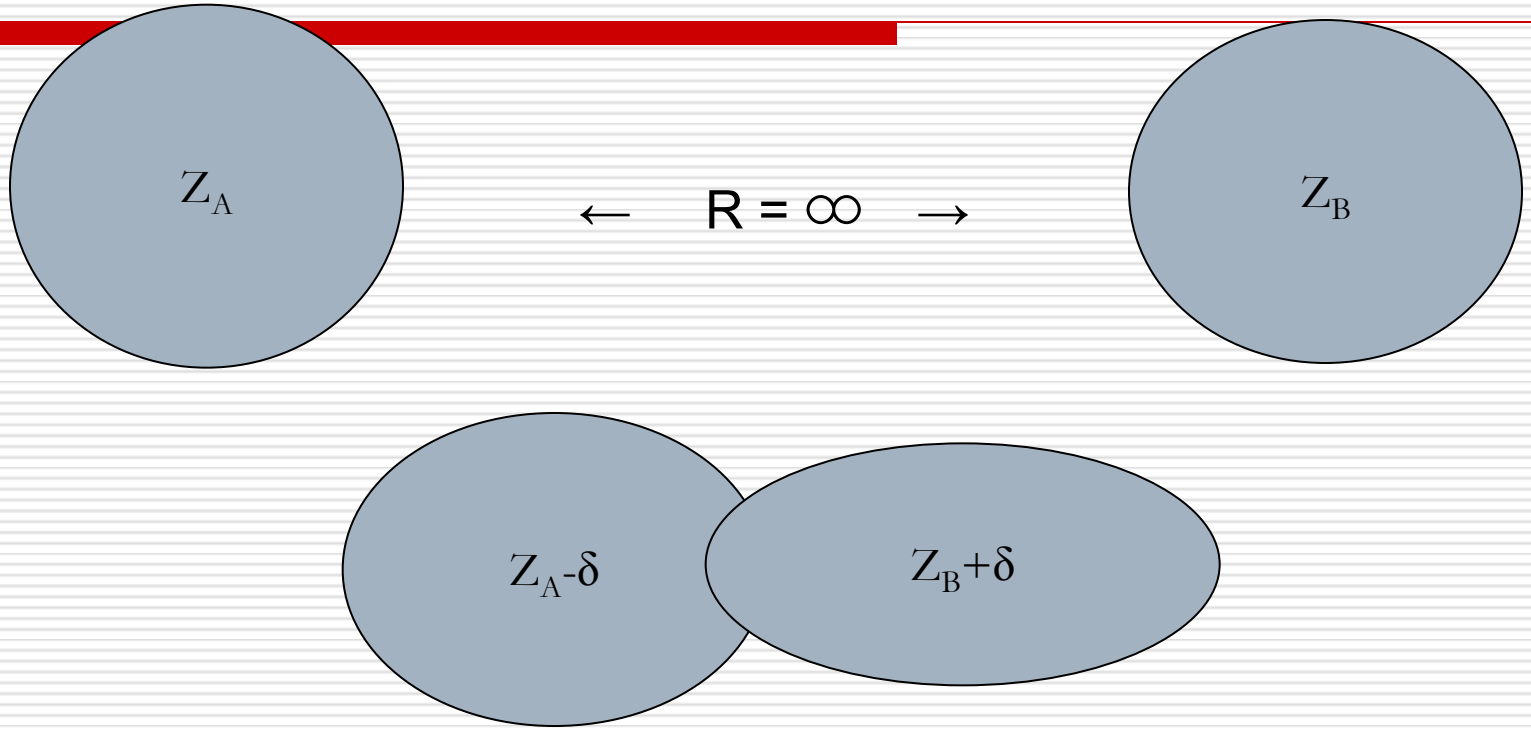
Schrödinger equation at the Born-Oppenheimer approach

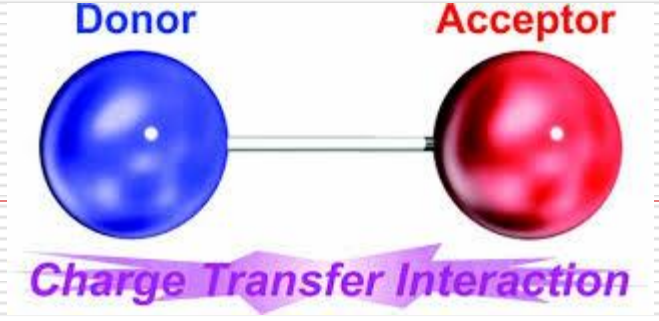
$$\hat{H} = -\frac{h^2}{8\pi^2}\sum_{A}^{\text{nuclei}}\frac{1}{M_A}\nabla_A^2 - \frac{h^2}{8\pi^2 m}\sum_{a}^{\text{electrons}}\nabla_a^2 - e^2\sum_{A}^{\text{nuclei}}\sum_{a}^{\text{electrons}}\frac{Z_A}{r_{Aa}}$$

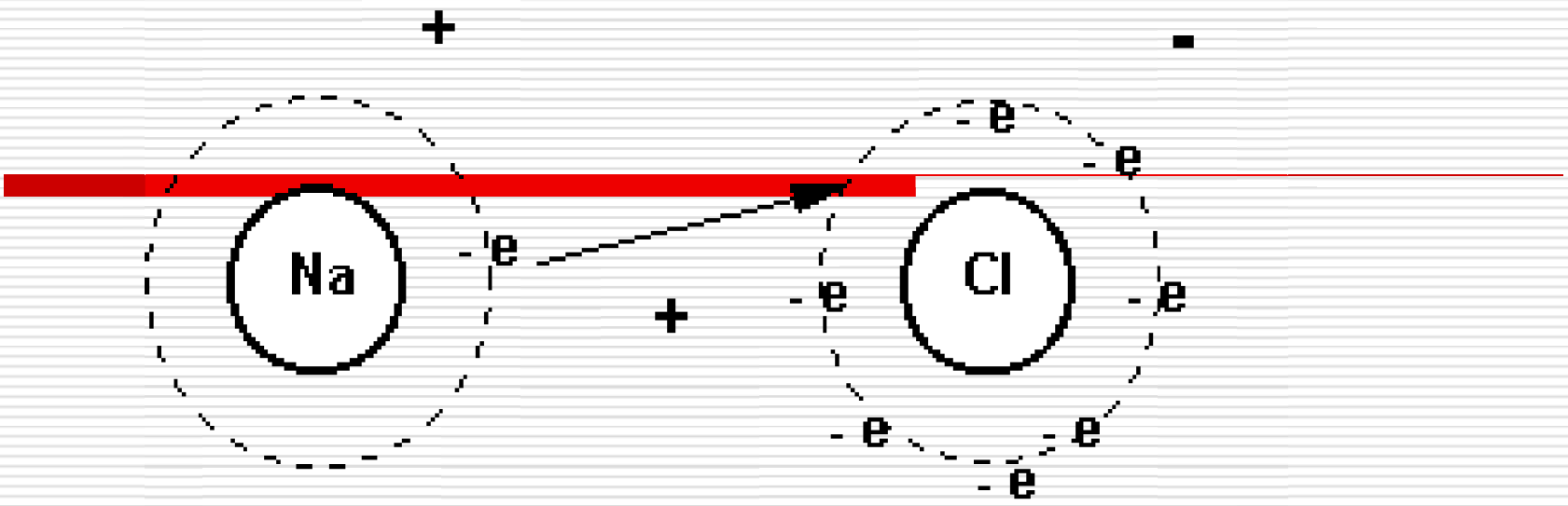
$$+ e^2\sum_{A>B}^{\text{nuclei}}\sum\frac{Z_A Z_B}{r_{AB}} + e^2\sum_{a>b}^{\text{electrons}}\sum\frac{1}{r_{ab}}$$

$$= \Sigma_a\, h(a) + \Sigma_{a,b}\, v(a,b)$$

Todo proceso fisicoquímico a nivel microscópico se caracteriza por una **TRANSFERENCIA de CARGA**






+
-
Na
e
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Cl
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e
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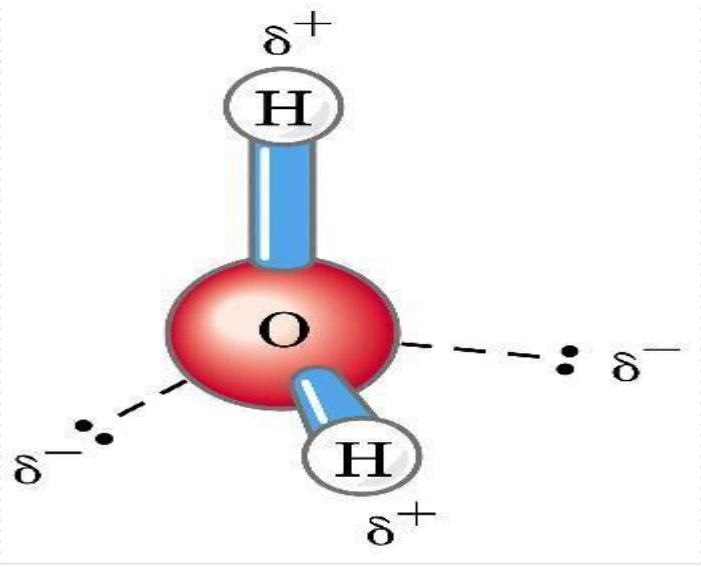
e
e


δ+
H
O
δ−
δ−
H
δ+

Chemical descriptors
Empirical ideas

- Covalent bond orders (shared electrons)
- Covalency – ionicity (complementary)
- Atomic charges (concept of particles)
- Valence
- Free valence (concept of holes)

associated with the electron density
(population analysis)
↔
partition of the number of electrons in the system, **N** (an integer number)

Among others … the list is not complete

Other fundamental descriptors

- Reactivity (vacant density sites)
- Electronegativity
- Chemical potential
- Others

associated with energy and electron density derivatives

a non integer number of particles, N

Problems: energy and electron distribution

- System
- States
- Energy determination

The system

Se necesita una definición y su caracterización de lo que sea un Átomo en una Mólecula (AIM)

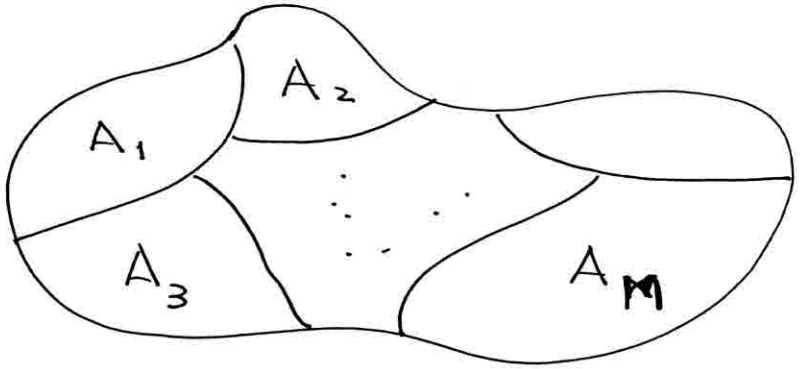
Formulaciones

1. Mulliken (base de orbitales atómicos, espacio de Hilbert)

2. Modelos "Fuzzy": dominios en el espacio físico (regiones) de soporte empírico

3. La aproximación Lagrangiana para la definicón de los dominios (Bader). Define una topología en forma rigurosa.

ATOMS IN MOLECULES (arbitrary definitions)



$\mathcal{M}$ (molecule)

- $A_1, A_2, \ldots, A_M$ (DOMAINS)

PHYSICAL SPACE

- $\mathcal{M} = \bigcup_{k=1}^{M} A_k$ $\qquad A_i \cap A_\ell = \begin{cases} \phi \text{ (empty)} \\ \neq \phi \end{cases}$

- each $\{A_\ell\}$ is an **OPEN SYSTEM**

$N = N + \nu$

$N \in \mathbb{Z}^+ ; \quad 0 \leq \nu \leq 1$

The states

DENSITY MATRICES (DM)

$$ {}^{N}D_{\Phi_k^N} = |\Phi_k^N >< \Phi_k^N| $$

$$ D = \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} |\Phi_k^M >< \Phi_k^M|; \qquad \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} = 1; \qquad \omega_{\Phi_k^M} \geq 0 $$

$$ D = \bigoplus_{\{\Phi_k^M\}}^{\infty} \omega_{\Phi_k^M} \; {}^{M}D_{\Phi_k^M} $$

Grand-canonical state

- finite trace, $tr(\mathcal{D}) < \infty$; normalization: $tr(\mathcal{D}) = 1$
- $\mathcal{D} = \mathcal{D}^{\dagger}$; hermiticity
- $\mathcal{D} \geq 0$; positive semi-definite

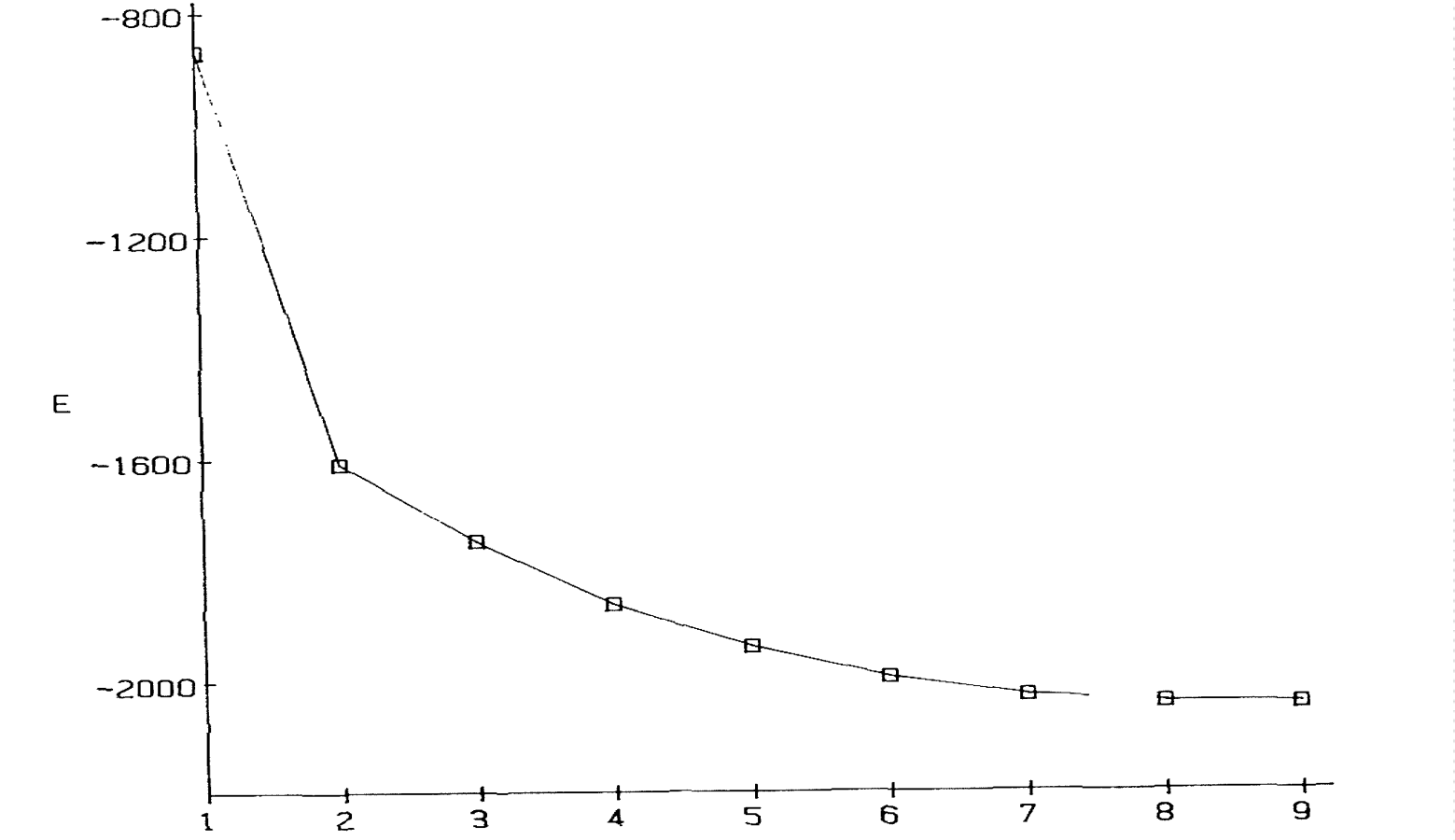
Probabilistic interpretation

$$\int dx_1 \int dx_2 \ldots dx_N \, {}^{N}\mathcal{D}\left(x_1, x_2, \ldots, x_N | x_1, x_2, \ldots, x_N\right) = 1$$

System energy

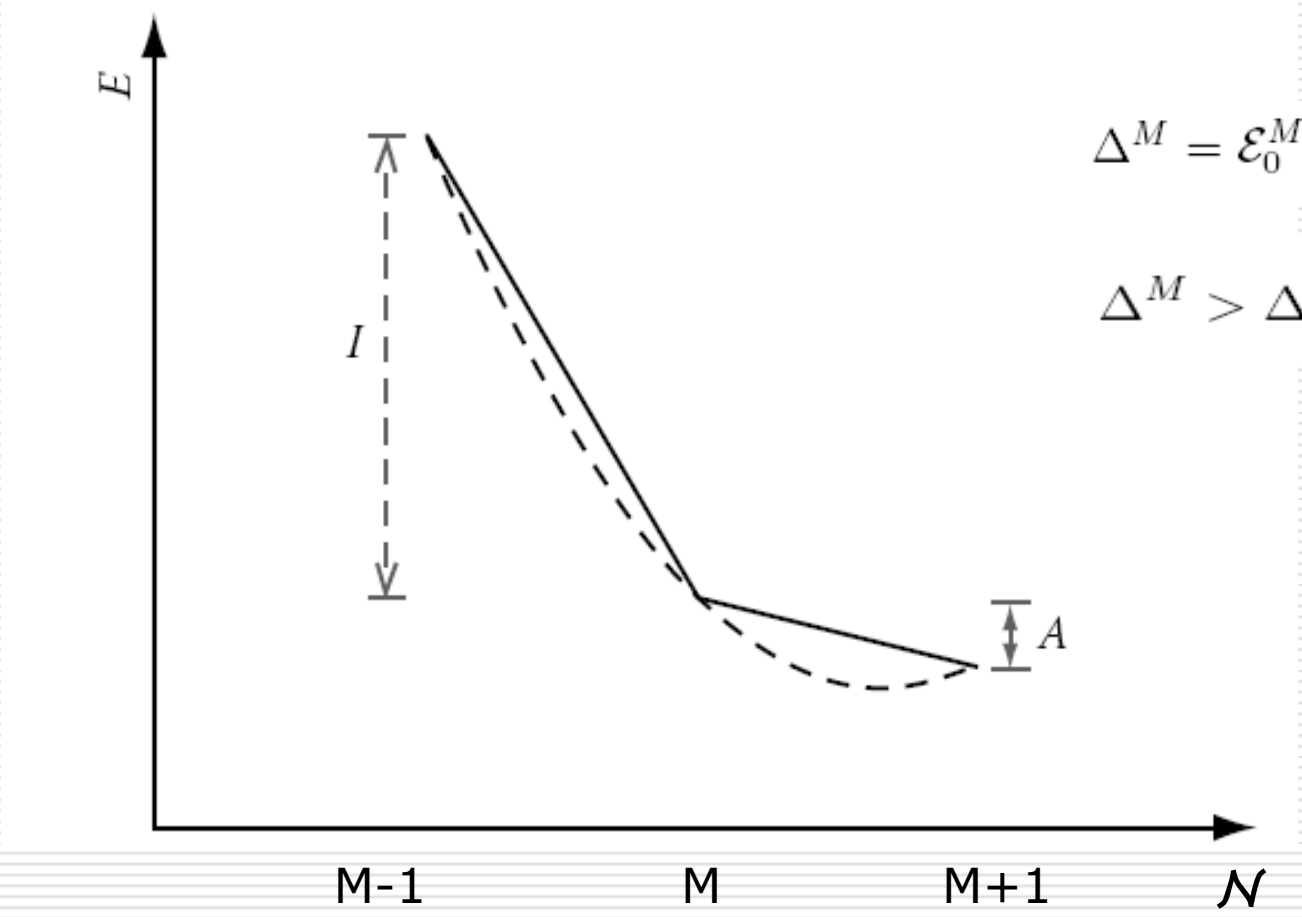
$$\mathcal{E} \;=\; \mathrm{Tr}\,(D\,\mathcal{H}) \;=\; \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M}\,\mathrm{Tr}\left({}^{M}D_{\Phi_k^M}\,\mathcal{H}\right)$$

The energy of an atomic or molecular system as a function of the number of electrons (arbitrary units)
Experimentally and numerically



Example: Oxygen atom and its ions

- *The energy is convex* ***(Hypothesis)***



$$\Delta^M = \mathcal{E}_0^{M-1} - \mathcal{E}_0^M$$

$$\Delta^M > \Delta^{M+1} > 0$$

Then it follows, (Lemma and Proposition (de la Oveja Rial))

Lemma 1. *For the sequence* $\left\{\mathcal{E}_0^M\right\}_{M\in\mathbb{N}}$ *verifying the above inequality, and arbitrary* $N, M \in \mathbb{N}$ *numbers, such that* $M \neq N, N+1$, *then*

$$\mathcal{E}_0^M \geq (N+1-M)\,\mathcal{E}_0^N + (M-N)\,\mathcal{E}_0^{N+1}$$

The equality holds iff $M = N, N+1$.

mathematical basis of the energy convexity

The ground state energy for the system with non integer number of particles is obtained from

$$\begin{cases} \min \mathcal{E} = \sum\limits_{\{\Phi_k^M\}} \omega_{\Phi_k^M} \operatorname{Tr}\left({}^{M}D_{\Phi_k^M}\, \mathcal{H} \right) \\ \sum\limits_{\{\Phi_k^M\}}^{\infty} \omega_{\Phi_k^M} M = N + \nu \end{cases}$$

With solution

Proposition 1. *The solution of this problem, i.e.,* $D = \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} \, {}^M D_{\Phi_k^M}$ *where the variational parameters are the statistical weights* $\{\Phi_k^M\}$*, is unique and become expressed by*

$$D = (1-\nu) \, {}^N D_0 + \nu \, {}^{N+1} D_0$$

A convex combination of only two pure state distributions: N and (N+1)- particles, leading to the energy

$$\mathcal{E}_0^{N+\nu} = (1-\nu)\,\mathcal{E}_0^N + \nu \mathcal{E}_0^{N+1}.$$

Las propiedades del sistema dependen exclusivamente de las densidades de partículas y de pares debido a que los correspondientes operadores son de 1- y 2-partículas.

↓

Por ello son necesarias las distribuciones marginales de la distribución *D*

p-order Reduced Density Matrices (p-RDM)

- Marginal distributions
- Contraction mapping from the DM

p-reduced density matrix (p-RDM)

$$\overbrace{{}^{p}\Gamma(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p | \mathbf{x'}_1, \mathbf{x'}_2, \ldots, \mathbf{x'}_p)} =$$

contraction mapping $\longrightarrow$ *average* $\longrightarrow$ *marginal distribution*

$$\overbrace{\int \mathrm{d}\mathbf{x}_{p+1} \ldots \int \mathrm{d}\mathbf{x}_N} \, {}^{N}\mathcal{D}\,(\mathbf{x}_1, \ldots, \mathbf{x}_p \mathbf{x}_{p+1}, \ldots, \mathbf{x}_N | \mathbf{x'}_1, \ldots, \mathbf{x'}_p \mathbf{x}_{p+1}, \ldots, \mathbf{x}_N)$$

$$\equiv \; tr_{p+1,\ldots,N}({}^{N}\mathcal{D})$$

- finite trace, $tr({}^pD) < \infty$; normalization: $tr({}^pD) = \binom{N}{p}$
- ${}^pD = {}^pD^\dagger$; hermiticity
- ${}^pD \geq 0$; positive semi-definite
- N-representability

$$\textit{Physical meaning} \rightarrow {}^p\mathcal{D} = \binom{N}{p}\,{}^p\Gamma; \qquad tr({}^p\mathcal{D}) = \binom{N}{p}$$

$$\downarrow$$

Densities: populations (diagonal elements) and coherences (off-diagonal)

$$p = 1, 2, \ldots,$$

$${}^1\mathcal{D} = N\,{}^1\Gamma; \qquad tr({}^1\mathcal{D}) = N$$

$${}^2\mathcal{D} = \binom{N}{2}\,{}^2\Gamma; \qquad tr({}^2\mathcal{D}) = \binom{N}{2}$$

Contraction mapping in Fock space

$$ {}^{p}D = \hat{L}_p\{D\} = \bigoplus_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M} \binom{M}{p} \hat{L}_M^p\{{}^{M}D_{\Phi_k^M}\} $$

$$ \hat{L}_p^p\{{}^{p}D_{\Phi_k^p}\} = \mathcal{I} $$

$$ \hat{L}_M^p\{{}^{M}D_{\Phi_k^M}\} = \mathbf{O} \; for \; M < p, $$

Identity superoperator

Null superoperador

Consequences

- **Energy functionals**

$$\mathcal{E}_0^{N+\nu} = \mathcal{F}({}^2D_o^{N+1}, {}^2D_o^N, \nu)$$

not

$${}^2D = (1-\nu)\,{}^2D_o^N + \nu\,{}^2D_o^{N+1}$$

- **Derivatives**

1. Chemical potential $\mu = \left(\frac{\partial \mathcal{E}_o^{\mathcal{N}}}{\partial \mathcal{N}}\right)_v$

$$\mu_{\pm} = \pm \left(\frac{\partial \mathcal{E}_o^{\mathcal{N}}}{\partial \nu}\right)_v = \pm \left(\mathcal{E}_0^{N\pm 1} - \mathcal{E}_0^{N}\right)$$

$$\mu_+ = \mathcal{E}_0^{N+1} - \mathcal{E}_0^{N} = -EA$$

$$\mu_- = \mathcal{E}_0^{N} - \mathcal{E}_0^{N-1} = -IP$$

Average ν electrons are removed or attached to the system

$$IP^{\nu} = \nu\, IP \qquad EA^{\nu} = \nu\, EA$$

2. Local descriptors: Fukui functions

$$f^{\pm}(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathcal{N}}\right)^{\pm}_{v}$$

$$F^{\pm}(\mathbf{r}|\mathbf{r}') = \pm\left(\frac{\partial}{\partial \omega}{}^{1}D^{N\pm\omega}(\mathbf{r}|\mathbf{r}')\right)_{v}$$

$${}^{1}D^{N\pm\nu} = \nu\,{}^{1}D^{N\pm 1} + (1-\nu)\,{}^{1}D^{N}$$

$$F^{\pm}(\mathbf{r}|\mathbf{r}') = \pm\left({}^{1}D^{N\pm 1}(\mathbf{r}|\mathbf{r}') - {}^{1}D^{N}(\mathbf{r}|\mathbf{r}')\right)$$

Final remarks

1. GC ideas: few particle open systems in their ground states.

2. Only two pure states contribute to the electron distribution of N+ν particle systems. Convex combination of N y N+1 states.

3. Contraction mapping for density matrices: p-RDM

4. Chemical local and non local descriptors in terms of p-RDMs valid for any type of state function.

5. Second order derivatives are coming