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Note: Energy convexity and density matrices in molecular systems

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From the onset of the Perdew, Parr, Levy, and Balduz (PPLB)¹ proposal for the energy of a molecular system involving a non-integer number of electrons and its immediate consequences, several applications have become familiar within the density functional theory (DFT) formalism.² However, to our knowledge, no attempts have been made to justify its use for other type of state-functions from which the electron density is derived, i.e., beyond DFT. Our main purpose here is to derive the above mentioned proposal by making use of the energy convex property of the energy for Coulombic interactions in atomic and molecular systems, extending the treatment to the most general form of the density matrix of the system for any type of state-function. In what follows we will adopt the following notations:

- (1) \mathcal{F}_M : M –particle Hilbert space,
- (2) $\mathcal{F} = \bigoplus_{M=0}^{\infty} \mathcal{F}_M$: Fock space,
- (3) $|\Phi_k^M\rangle$: k th M -electron pure state of a M -electron system in the antisymmetric M -electron Hilbert space; Hamiltonian eigenstates,
- (4) $D = \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} |\Phi_k^M\rangle \langle \Phi_k^M|$, $\sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} = 1$, $\omega_{\Phi_k^M} \geq 0$: density matrix (DM) defining the states of the system (grand-canonical type),
- (5) ${}^N D = \sum_{\Phi_k^N} \omega_{\Phi_k^N} |\Phi_k^N\rangle \langle \Phi_k^N|$; $\sum_{\Phi_k^N} \omega_{\Phi_k^N} = 1$; $\omega_{\Phi_k^N} \geq 0$ (canonical type), and
- (6) ${}^N D_{\Phi_k^N} = |\Phi_k^N\rangle \langle \Phi_k^N|$ (micro-canonical or pure state) and $\omega_{\Phi_k^M}$ the corresponding statistical weights for each $|\Phi_k^M\rangle$ pure state.

To describe the energy dependence of the system with the particle number let us introduce the most general state, which admits a non-integer number of particles, by means of a density matrix in Fock space, $D \in \bigoplus_{M=0}^{\infty} \mathcal{F}_M$. The energy determined as the average of the Hamiltonian over this distribution is given by^{3,4}

$$\bar{\mathcal{E}} = \text{Tr}(D \mathcal{H}) = \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} \text{Tr}({}^M D_{\Phi_k^M} \mathcal{H}), \quad (1)$$

where \mathcal{H} stands for the Hamiltonian operator of the system and Tr for the mathematical trace operation. Let ${}^M D_0$ be the DM of a non-degenerate or removable degenerate ground state^{5,6} of the M -particle system, $\mathcal{E}_0^M = \text{Tr}({}^M D_0 \mathcal{H})$, its energy and $\Delta^M = \mathcal{E}_0^{M-1} - \mathcal{E}_0^M$, the lowest energy difference, i.e., the first ionization potential of the atomic or molecular system.

Assuming $M > 1$, the inequality, $\Delta^M > \Delta^{M+1} > 0$, i.e., the convex hypothesis for the molecular energy,^{1,2} implies the following.

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

$$\mathcal{E}_0^M \geq (N+1-M)\mathcal{E}_0^N + (M-N)\mathcal{E}_0^{N+1}. \quad (2)$$

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

Proof. It is immediate to see that the equality holds for $M = N, N+1$. Let us consider the case for $M = N+1+p$, $p \in \mathbb{N}$, $p > 1$. We will derive the above statement by applying the induction procedure for the variable p . For $p = 1$, i.e., $M = N+2$, and $\Delta^{N+1} > \Delta^{N+2}$, $\mathcal{E}_0^{N+2} > -\mathcal{E}_0^N + 2\mathcal{E}_0^{N+1}$ follows; then the hypothesis $\Delta^{N+1} > \Delta^{N+2+p}$, leads to

$$\mathcal{E}_0^{N+2+p} > \mathcal{E}_0^{N+1+p} + \mathcal{E}_0^{N+1} - \mathcal{E}_0^N,$$

which jointly with the inductive hypothesis lead to

$$\begin{aligned} \mathcal{E}_0^{N+2+p} &> (p+1)\mathcal{E}_0^{N+1} - p\mathcal{E}_0^N + \mathcal{E}_0^{N+1} - \mathcal{E}_0^N \\ &= (p+2)\mathcal{E}_0^{N+1} - (p+1)\mathcal{E}_0^N, \end{aligned}$$

which probes the case for $M > N+1$. To complete this derivation let us consider the case $M = N-p$; hence for $p = 1$ it follows that $\mathcal{E}_0^{N-1} > 2\mathcal{E}_0^N - \mathcal{E}_0^{N+1}$ and also applying the inductive method, it follows that

$$\begin{aligned} \mathcal{E}_0^{N-p-1} &> \mathcal{E}_0^{N-p} + \mathcal{E}_0^N - \mathcal{E}_0^{N+1} \\ &> (p+1)\mathcal{E}_0^N - p\mathcal{E}_0^{N+1} + \mathcal{E}_0^N - \mathcal{E}_0^{N+1} \\ &= (p+2)\mathcal{E}_0^N - (p+1)\mathcal{E}_0^{N+1}, \end{aligned}$$

which completes the derivation. \square

Equation (2) is the expression of the convexity for the energy; hence to obtain the ground state energy for the system of a non-integer number, $N + \nu$ with $N \in \mathbb{N}$ and $\nu \in (0, 1)$ we may use the variational principle introducing explicitly the number of particles as a constrain in the following way:

$$\left\{ \begin{array}{l} \min \mathcal{E} = \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} \text{Tr}({}^M D_{\Phi_k^M} \mathcal{H}) \\ \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} M = N + \nu. \end{array} \right. \quad (3)$$

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 $\{\omega_{\Phi_k^M}\}$, is unique and become expressed by

$$D = (1 - \nu) {}^N D_0 + \nu {}^{N+1} D_0. \quad (4)$$

Proof: Regarding the inequality $\mathcal{E}_0^M \leq \text{Tr}({}^M D_{\Phi_k^M} \mathcal{H})$, for the ground state of the system, and adding over the whole Fock space of the ground states, it follows:

$$\sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} \mathcal{E}_0^M = \sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} \text{Tr}({}^M D_0 \mathcal{H}) \leq \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} \text{Tr}({}^M D_{\Phi_k^M} \mathcal{H}),$$

and assuming the hypothesis that the ground states are non-degenerate or removable degenerate,^{5,6} the minimum value only can be reached by a convex combination of these ground states. Then from Lemma 1,

$$\begin{aligned} \sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} \mathcal{E}_0^M &\geq \sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} (N + 1 - M) \mathcal{E}_0^N \\ &+ \sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} (M - N) \mathcal{E}_0^{N+1} \\ &= (1 - \nu) \mathcal{E}_0^N + \nu \mathcal{E}_0^{N+1} \end{aligned} \quad (5)$$

is obtained, where we have defined two convex coefficients as $\sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} (N + 1 - M) = 1 - \nu$ and $\sum_{\{\Phi_\sigma^M\}} \omega_{\Phi_\sigma^M} (M - N) = \nu$, because of the hypothesis constraint for the number of particles. Also for any $M \neq N, N + 1$ and their associated $\omega_{\Phi_\sigma^M} > 0$, the inequality would be strict and then the proof is complete. \square

Therefore, the rhs of Eq. (5) stands for the energy of the systems with non-integer number of particles, $N + \nu$ which reads as

$$\mathcal{E}_0^{N+\nu} = (1 - \nu) \mathcal{E}_0^N + \nu \mathcal{E}_0^{N+1}. \quad (6)$$

Equation (6) constitutes the PPBL proposal for the energy involving a non-integer number of particles but in the present case, as no hypothesis has been invoked about the approach to obtain the state functions, the results in this report are valid for any type of state-function and consequently for the corresponding DM structure⁷ expressed by Eq. (4), i.e., independent particle or correlated.

The units in the molecular structure, i.e., physical domains likewise atoms, functional groups or moieties, share the feature of possessing a non-integer number of electrons, which may be interpreted as a time average in a given quantum state of an open system and because they are involved in the chemical processes, essentially exchange electrons between them.¹ Hence, the description of the behaviour of such domains is performed not only by means of their fundamental magnitudes like the energy and density, but also their derivatives, as chemical potential, Fukui functions (reactivity), electronegativity, among others,² which are the adequate physico-chemical magnitudes that naturally incorporate the mentioned changes in the number of particles and are at the very basis of the definitions of these descriptors.² Therefore, beyond DFT, the proper scenario for the description of the electronic changes is that of the reduced density matrices, p -RDMs⁶ which in this case are obtained by the contracting mapping of the grand-canonical DM⁸ and then it opens the way to generalize the mentioned descriptors in terms of the RDMs. Consequently, this form also enables incorporating the effects of correlation in an explicit way to them. Work in this direction is being carried out in our laboratory.

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