

Completely soft molecular electrostatic potentials (CoSMEP) and total density functions

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Received: 1 March 2013 / Accepted: 3 April 2013 / Published online: 11 April 2013
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Abstract Soft molecular electrostatic potentials (SMEP or SEMP) have been recently defined substituting the point-like proton by a Gaussian positive charge distribution. In the present paper an additional step is taken forward, transforming SMEP into a completely soft MEP (CoSMEP). Such transformation is carried out using a charge distributed proton as in SMEP and also a Gaussian positive nuclear charge distribution, instead of the classical point-like nuclear charges. The general form of MEP is roughly preserved, but new features can be noticed. Such new point of view is also associated to the possibility to redefine the molecular charge density. Definition of CoSMEP is thus connected to the definition of total molecular density functions (DF), where to the negative electronic DF is summed up the soft nuclear DF, made of linear combinations of Gaussian distributions of nuclear charges.

Keywords Molecular electrostatic potential (MEP) · Soft MEP (SMEP) · Completely soft MEP (CoSMEP) · Soft Gaussian nuclear charge distribution · Total density function

1 Introduction

Molecular electrostatic potentials (MEP), were originally described by Scrocco and coworkers¹, see for instance reference [1]. The concept has not evolved very much

¹ Initially the term used by these authors was electrostatic molecular potential (EMP). As an homage to Professor Scrocco we preserved the original naming and acrostic, appearing in the previous papers on the soft EMP subject. With time the name has changed to molecular electrostatic potential (MEP) and from now on, the name and acrostic it will be adopted in this form.

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from the original times form, but multiple applications have been described, see for example the assorted references [2–12]. Nowadays MEP can be considered as a routinely employed quantum chemical tool.

Because of quantum similarity measure computational needs, see for instance references [13–15] the so-called atomic shell approximation (ASA) to construct simple molecular density functions (DF) has been described and used in many instances, see references [16,17]. Some old studies were performed on employing ASA to compute MEP, see reference [18]. Recently, some renewed interest in the connection of EMP with ASA has been put forward [19]. More recently, two papers, devoted to the description of soft MEP (SMEP)² [20,21], have been published. SMEP was straightforwardly calculated just substituting the interacting proton by a Gaussian distribution, while preserving the point-like molecular nuclear charge distribution.

In the present study it will be proposed to take a new step forward, based on a previous study [22], by substituting the positive nuclear point-like charges by a soft positive nuclear charge distribution, made of a linear combination of normalized Gaussian functions, whose coefficients are the nuclear charges. In this way a total DF can be also defined summing up the nuclear contribution to the electronic DF. The resulting MEP, computed through the interaction of a soft proton with the total DF, will be named as completely soft MEP or CoSMEP.

In order to achieve this computational project at the stage of its mathematical development, the present paper will be organized in the following way. First the construction of soft Gaussian nuclear charge distributions will be discussed. Then CoSMEP will be defined and the needed integrals over Gaussian functions will be provided. Finally, some graphical examples of CoSMEP will be presented and a discussion on the main features encountered given.

2 Soft nuclear charge distributions and density functions

As a starting point of this study it will be discussed the construction of a nuclear charge distribution on a continuous basis, instead of the classical point-like distribution used within the Born–Oppenheimer approximation [23].

2.1 Classical hard Dirac's nuclear charges distribution

Point-like molecular nuclear charge distributions under Born–Oppenheimer approximation, can be described using a linear combination of a Dirac distributions set, see for example [24], centered at the nuclear sites in a given arbitrary molecular frozen conformation. This situation can be written, for instance, using the expression:

$$\rho_D(\mathbf{r}) = \sum_I^N Z_I \delta(\mathbf{r} - \mathbf{R}_I), \quad (1)$$

² Due to the dual nomenclature, described in the previous footnote, the previous papers on soft MEP in our laboratory have named the soft electrostatic potentials as SEMP, instead of SMEP, a new term which will be used from now on.

where N is the number of involved atoms, $\{Z_I | I = 1, N\}$ are the nuclear charges and $D = \{\delta(\mathbf{r} - \mathbf{R}_I) | I = 1, N\}$ is a set of Dirac's delta functions centered at the atomic positions: $\{\mathbf{R}_I | I = 1, N\}$. Each function in the set D is Minkowski normalized, that is integrates over the whole space to unity:

$$\forall I : \langle \delta(\mathbf{r} - \mathbf{R}_I) \rangle = \int_D \delta(\mathbf{r} - \mathbf{R}_I) d\mathbf{r} = 1$$

Such nuclear charge distribution or DF written like in Eq. (1) can be considered equivalent to describe a set of positive nuclear charges possessing no space extension.

2.2 Soft Gaussian nuclear charges distribution

Nothing opposes, though, to transform the point-like nuclear charge distribution (1) into a Gaussian charge distribution, using a set of Minkowski normalized Gaussian distributions which can be defined as: $G = \{\gamma(\alpha | \mathbf{r} - \mathbf{R}_I) | I = 1, N\}$, and that one can suppose constructed with an uniform exponent α as follows:

$$\begin{aligned} \forall I : \gamma_I &\equiv \gamma(\alpha | \mathbf{r} - \mathbf{R}_I) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right) \rightarrow \\ \langle \gamma_I \rangle &= \int_D \gamma(\alpha | \mathbf{r} - \mathbf{R}_I) d\mathbf{r} = 1. \end{aligned}$$

When the Gaussian exponent tends to infinite, the set G has as a limit the Dirac's distribution set described in D . This is so because the well-known Gaussian-Dirac distribution relationship holds:

$$\forall I : \lim_{\alpha \rightarrow \infty} \gamma(\alpha | \mathbf{r} - \mathbf{R}_I) = \delta(\mathbf{r} - \mathbf{R}_I).$$

Then, the equivalent of the Dirac's nuclear DF (1), can be generally rewritten in terms of the Gaussian nuclear DF:

$$\begin{aligned} \rho_G(\mathbf{r}) &= \sum_I^N Z_I \gamma(\alpha | \mathbf{r} - \mathbf{R}_I) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_I^N Z_I \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right) \\ &= \sum_I^N Z_I \gamma_I \end{aligned} \quad (2)$$

with the additional properties:

$$\lim_{\alpha \rightarrow \infty} \rho_G(\mathbf{r}) = \rho_D(\mathbf{r}) \rightarrow \langle \rho_G \rangle = \sum_I Z_I = v = \langle \rho_D \rangle,$$

where ν is the number of electrons in the neutral molecule. Equation (2) also shows that the Minkowski normalization factor, which have been chosen as common to all the Gaussian elements in the linear combination (2), acts as a scale factor of the Gaussian nuclear DF.

Two characteristic points might be noted in connection of the above definitions.

First, while the classical Dirac DF (1) can be named as *hard* nuclear charge DF, the family (2) can be named as *soft* nuclear charge DF's, according to the nomenclature put forward in earlier work [20,21], when dealing with a soft proton charge distribution as generating SMEP.

Second, the localized weight of the Gaussian nuclear charge DF in the neighborhood of every nucleus, is manifestly associated to the magnitudes of the nuclear charge itself and the choice of the Gaussian exponent. In fact, the Gaussian exponent as it grows produces a harder, more localized, charge distribution. Approximately a sphere of radius $r = 2\alpha^{-1}$ au contains around a 95% of the associated atomic charge. Then, taking a Carbon atom as an example, using $\alpha = 2$ implies that a charge of around 5.7 is contained into a sphere of one au radius.

2.3 Total soft molecular density function

Moreover, the finite structure of the Gaussian nuclear charge DF of type (2) everywhere in space, permits to consider the possibility to define a total molecular DF: $\rho_T(\mathbf{r})$ by means of adding the electronic DF: $\rho_e(\mathbf{r})$ to the nuclear charges distribution: $\rho_G(\mathbf{r})$, that is:

$$\rho_T(\mathbf{r}) = \rho_G(\mathbf{r}) - \rho_e(\mathbf{r}). \quad (3)$$

Because of this definition, in neutral molecular structures, the molecular total DF has a null Minkowski pseudonorm, as one can easily compute the involved integrals in the form:

$$\langle \rho_T \rangle = \langle \rho_G \rangle - \langle \rho_e \rangle = \nu - \nu = 0.$$

2.4 Overlap selfsimilarity in soft total density functions

Overlap selfsimilarity integrals for quantum objects correspond to a well-defined numerical quantity associated to quantum similarity, see for example references [13,14]. It corresponds in the present context to the integral of the Euclidean norm of the total soft molecular DF, that is:

$$\theta_T = \langle |\rho_T|^2 \rangle = \langle |\rho_G|^2 \rangle + \langle |\rho_e|^2 \rangle - 2 \langle \rho_G \rho_e \rangle = \theta_G + \theta_e - 2\Theta_{Ge}, \quad (4)$$

where the symbol θ is used to denote selfsimilarity and the corresponding capital Θ as representing the similarity integral between two DF, see for example [14].

An interpretation of the above result can be done as follows. The two first terms of Eq. (4) correspond to the nuclear and electronic selfsimilarities associated to both

involved DF, while the third one corresponds to the similarity integral between the soft Gaussian nuclear distribution and the electronic DF. Moreover, the total selfsimilarity resulting expression can be also associated to a squared Euclidian distance: D_{Ge}^2 between the two DF components, because it can be also written:

$$D_{Ge}^2 = \langle |\rho_G - \rho_e|^2 \rangle = \theta_T. \quad (5)$$

The total selfsimilarity definition in Eq. (4) will become zero if and only if the two nuclear and electronic DF components become exactly the same function, that is: $\rho_G = \rho_e \rightarrow \langle \theta_T \rangle = 0$. Although this condition corresponds to a situation which hardly will be met, provided the oversimplified expression of the nuclear charge distribution (2). Considered as a squared Euclidian distance, total molecular selfsimilarity will be positive definite in any circumstance other than the one of nuclear and electronic DF coincidence. Therefore, because of this intrinsic positive definiteness, it will be equally certain that the following inequality will hold:

$$\theta_T \geq 0 \rightarrow \langle |\rho_G|^2 \rangle + \langle |\rho_e|^2 \rangle \geq 2 \langle \rho_G \rho_e \rangle.$$

Soft nuclear Gaussian DF selfsimilarity can be easily computed, taking into account that the overlap between two unnormalized Gaussian functions can be expressed as:

$$\begin{aligned} \forall I, J : \Theta_{IJ} &= \int_D \exp(-\alpha |\mathbf{r} - \mathbf{R}_I|^2) \exp(-\alpha |\mathbf{r} - \mathbf{R}_J|^2) d\mathbf{r} \\ &= \left(\frac{\pi}{2\alpha}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right), \end{aligned}$$

therefore using expression (2) one can write:

$$\langle |\rho_G|^2 \rangle = \left(\frac{\alpha}{\pi}\right)^3 \sum_I \sum_J Z_I Z_J \Theta_{IJ} = \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \sum_I \sum_J Z_I Z_J \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right).$$

In order to grasp a particular form of such a selfsimilarity measure attached to nuclear soft charge distributions, one can choose a homonuclear diatomic molecule as a particular test case. If the involved atoms have both charge Z and are located at a distance R , then the nuclear selfsimilarity could be written easily as:

$$\langle |\rho_G|^2 \rangle = 2Z^2 \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \left(1 + \exp\left(-\frac{\alpha}{2} R^2\right)\right).$$

2.5 Origin shift and total density functions

Recent research performed in our laboratory on origin shifting performed over DF sets resulted in several publications [25–30] dealing with the theoretical geometrical

background and the applications. It is obvious that the total DF definition, expressed as can be found in Eq. (3), corresponds to a natural origin shift of physical origin and issued from the respective charge distribution signs, which induce the Gaussian nuclear DF origin shift performed by the electronic DF. Although in reverse terms, it will be also valid from the geometrical point of view to speak of the origin shift of the electronic DF by means of the Gaussian nuclear DF. As a result of either point of view, the angle between both functions is meaningless [25,30], but not the Euclidian squared distance as defined in Eqs. (4) and (5).

All these interesting simple definitions and relationships could have not been specified within the classical Dirac's nuclear DF model, as written in Eq. (1). The origin of this extended set of properties of the total DF is founded on the assumption that the nuclear charges are no longer point-like, but extended within three dimensional space by some amount, which will depend upon the magnitude of the Gaussian exponent.

3 Completely soft electrostatic molecular potentials

After defining the total DF as in Eq. (3), the definition of CoSMEP is immediate. However, to complete the MEP definition, beforehand it must be well-defined the soft proton DF, see for example references [20,21], in the way the soft nuclear Gaussian DF has been constructed. A soft proton charge distribution centered at the three dimensional space position \mathbf{R}_H surrounding a given molecule, can be easily defined as the Minkowski normalized Gaussian function:

$$\rho_H(\mathbf{r}) = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \exp\left(-\beta |\mathbf{r} - \mathbf{R}_H|^2\right)$$

in the way it has been previously employed [21] when defining SMEP. Then, the CoSMEP can be computed with the Coulomb expression:

$$V(\mathbf{R}_H) = \left\langle \rho_T(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \rho_H(\mathbf{r}_2) \right\rangle = \int_D \int_D \frac{\rho_T(\mathbf{r}_1) \rho_H(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (6)$$

Of course, the CoSMEP in the above equation will have two parts, according to the definition of the total DF in Eq. (3), that is:

$$\begin{aligned} V(\mathbf{R}_H) &= V_G(\mathbf{R}_H) - V_e(\mathbf{R}_H) \\ &= \left\langle \rho_G(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \rho_H(\mathbf{r}_2) \right\rangle - \left\langle \rho_e(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \rho_H(\mathbf{r}_2) \right\rangle \end{aligned}$$

The electronic contribution $V_e(\mathbf{R}_H)$ might be exactly expressed as in the SMEP case [21] and thus will be not repeated here. The soft nuclear part $V_G(\mathbf{R}_H)$ is quite straightforward, as it will possess the structure of Coulomb repulsion between pairs of positive Gaussian charge distributions. The needed integrals implying every nucleus

interacting with the proton, are readily computed, as they correspond for the I -th nucleus to the simple expression:

$$\begin{aligned} \forall I : V_{GI} &= Z_I \left\langle \gamma(\alpha |\mathbf{r}_1 - \mathbf{R}_I|) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \rho_H(\mathbf{r}_2) \right\rangle \\ &= Z_I \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} \int_D \int_D \frac{\exp(-\alpha |\mathbf{r}_1 - \mathbf{R}_I|^2) \exp(-\beta |\mathbf{r}_2 - \mathbf{R}_H|^2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 2Z_I \left(\frac{\alpha\beta}{\pi(\alpha + \beta)} \right)^{\frac{1}{2}} F_0 \left(\frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_I - \mathbf{R}_H|^2 \right) \end{aligned}$$

where use is made of the incomplete gamma function: $F_0(t)$, see for example reference [31]. Thus, the needed integrals are well-defined and the corresponding CoSMEP easily available.

Practical use of the integral expressions demands besides computational simplicity, coherence about the nuclear density representation. In this sense the proton probe, considered as a hydrogen nucleus, cannot be different from the molecular hydrogen nuclei.

So, the two Gaussian exponents, which have been considered different for the sake of generality in the previous deduction yielding the above equation, one can also admit they might be the same: $\alpha = \beta$. Thus, the former above integral expression can be reduced to the simpler scaled incomplete gamma function:

$$V_{GI} = Z_I \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{2}} F_0 \left(\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_H|^2 \right).$$

The most interesting facet of CoSMEP, which the previous SMEP formulation also possessed [20,21], lies in the fact that when the proton is coincident with any nuclear position coordinate, that is: $\mathbf{R}_I = \mathbf{R}_H$, then the corresponding term V_{GI} remains finite as well as the total CoSMEP does.

Such a finite characteristic behavior is extremely important when two or more MEP, associated to different molecular structures, have to be compared in a similar way as DF are, within an appropriate quantum similarity theoretical formalism [13,14,28]. This issue will be studied elsewhere.

4 Some graphical examples of total DF and CoSMEP

In this section, several kinds of molecular maps will be shown for two chosen molecules. The ASA description [16,17] for electronic density functions has been chosen in all the examples. When representing the CoSMEP, due to the reasons already expressed, the two relevant exponents α and β as discussed in the previous paragraph, are set to be equal in each figure. For each series of DF maps, the electronic DF provides a unique map for each molecule, whereas nuclear and total DFs are depending on the chosen nuclear exponential parameter.

It must be also noted that the electronic DF by itself is non-positive definite, despite that here the given representation is shown in absolute value, when it is separately drawn. Regarding the nuclear and the total DFs, the first one is non-negative definite everywhere and the later in non-definite as it can be positive or negative depending on the spatial regions considered. In all the maps shown, each picture bears its own optimal scaling to make visualization easier.

Figure 1 shows a series of CoSMEP maps for 1-methoxy-2-nitrobenzene molecule. The values for the exponents $\alpha = \beta$ where set to 1, π and 10.

As it can be seen from Figure 1, increasing the exponential parameters leads to sharper MEP peaks. Such behavior appears because both the nuclear density and the probe proton charges become more localized. The chosen sequence of parameters provides a graphical deformation which tends to the classical point-like charges limit, where both exponents will be formally set to be infinite.

Figure 2 shows 1-methoxy-2-nitrobenzene electronic DF absolute values according to an ASA description. The total DF is obtained when the electronic DF is subtracted from the nuclear one. Figure 3 shows the nuclear and total DFs obtained for each value of the exponential parameter. One can note the obvious fact that while the exponential

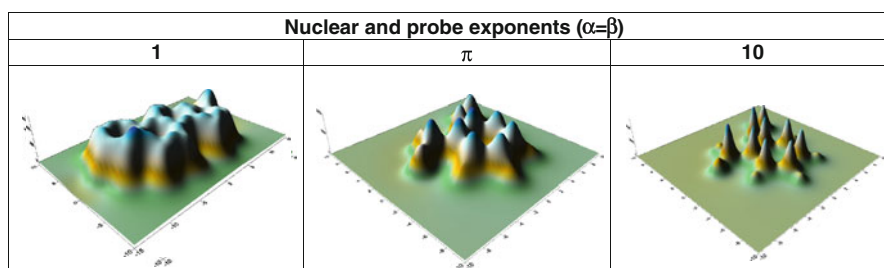


Fig. 1 CoSMEP for 1-methoxy-2-nitrobenzene. The values for $\alpha = \beta$ exponents are 1, π and 10. The representation is made by the computed potential function values on the molecular ring plane points

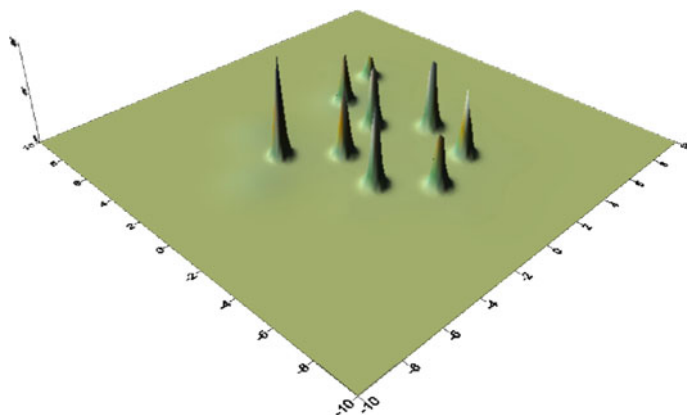


Fig. 2 Absolute value of the electronic DF for 1-methoxy-2-nitrobenzene. The representation is made with the DF values obtained on the ring plane points

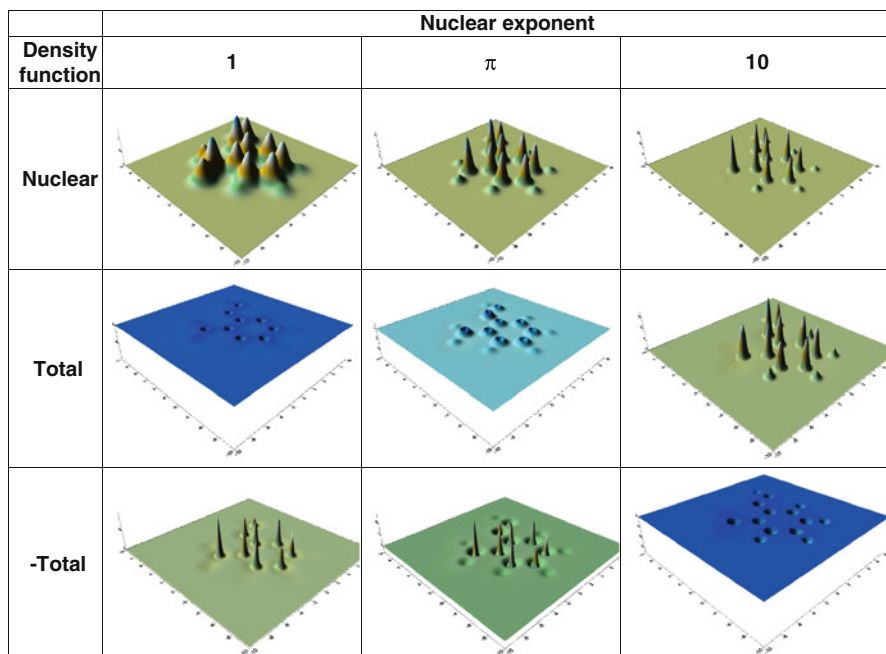


Fig. 3 Nuclear, total and sign reversed total DFs, obtained for each chosen exponential parameter for 1-methoxy-2-nitrobenzene. From left to right, in each column the nuclear exponent values are 1, π and 10. The representation is made with DF values computed on the molecular plane points

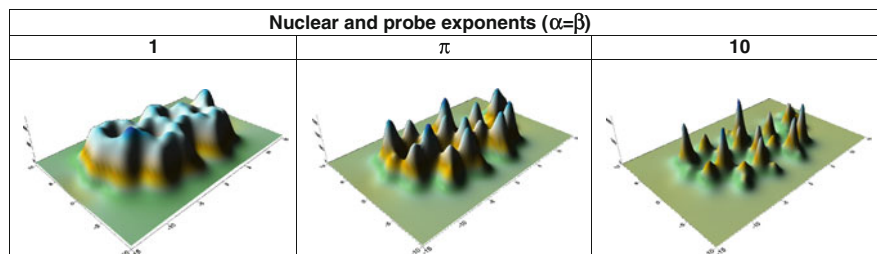


Fig. 4 CoSMEP representation for the molecule of aldosterone. The values for $\alpha = \beta$ exponents are 1, π and 10. The representation has been chosen with the potential function values within the points of the plane defined by the fused rings

parameters increase, the (positive) nuclear density increases and becomes the relevant part of the map. For the exponents 1 and π , the electronic DF, the negative part of the total DF, dominates. In order to visualize this effect, in Figure 3 it has been also represented with inverted sign the total DF.

In order to test both CoSMEP and total DF for a larger molecular structure, Figure 4 shows CoSMEP for the molecule of aldosterone computed with an electronic DF within an ASA scheme. The values for the exponents $\alpha = \beta$ have also set to 1, π and 10. The pictures show how, as expected, the same behavior, formerly noticed in the 1-methoxy-2-nitrobenzene case, is reproduced: the sharper MEP peaks appear for the

higher exponential parameter values. Therefore a continuation of this sequence will lead to the classical nuclear point-like charges limit.

Figure 5 shows the aldosterone electronic DF computed with an ASA model and Fig. 6 is the corresponding series of nuclear and total DFs. As in the former example, when the exponent is set to 1 the electronic part is the relevant one. On the other side, when the parameter is equal to π , for aldosterone the nuclear DF starts to be the relevant one.

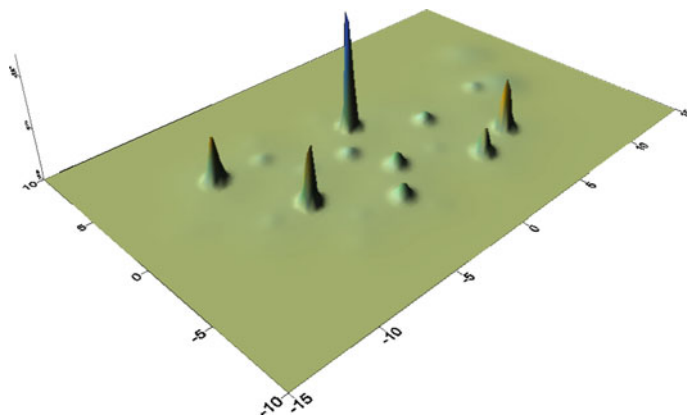


Fig. 5 Electronic DF for aldosterone along the points of the molecular plane defined by the fused rings

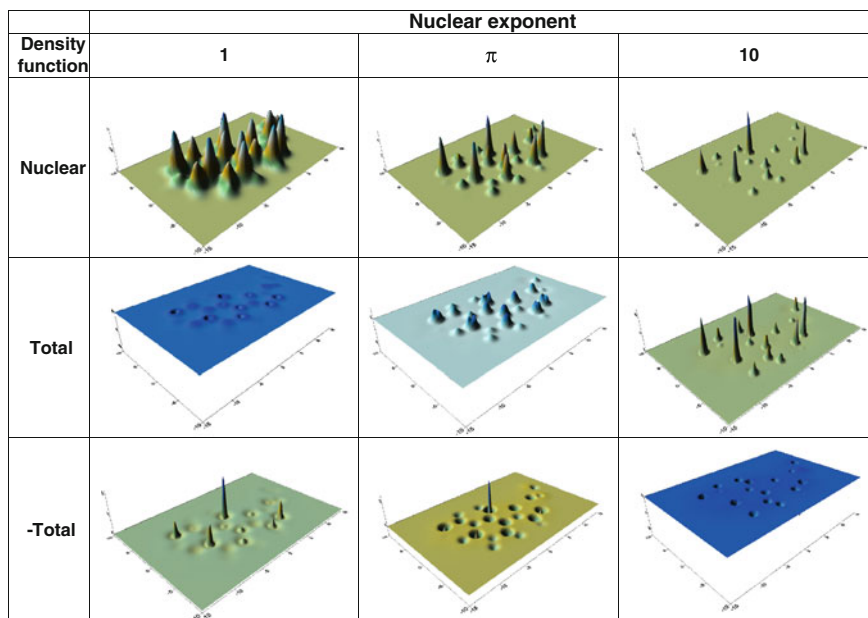


Fig. 6 Nuclear, total and sign reversed total DFs obtained for each exponential parameter for the aldosterone molecule. From *left to right*, in each column the nuclear exponent values are 1, π and 10. The representation is provided along the points of the molecular plane defined by the molecular fused rings

5 Discussion

Theoretical definition of CoSMEP and total DF has been also practically extended here with some practical computation leading to graphical examples. The presented results preclude that modified nuclear charge density functions might become useful quantum chemical tools.

From perusal of the provided examples it seems that both molecular functions can be employed within a range of values, associated to the nuclear charge distribution sharpness. Such possibility provides in the case of CoSMEP more fuzzy potential function patterns as the DF nuclear exponents are nearby the unit and localizes or sharpens them as the exponents are chosen larger. Such behavior must be certainly expected because, as larger the exponents are the nuclear DF becomes nearby the point-like nuclear charge limit.

Apparently, nothing opposes to use such Gaussian charge distribution approach to describe nuclear charge distributions in general, within a soft molecular structure definition, and in association with more accurate electronic *ab initio* DFs, which can safely substitute the present electronic ASA DF approach.

At any computational level CoSMEP functions will be anywhere finite.

In this way, the possibility of quantum similarity technical comparison of two or more CoSMEP has been also set up.

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