

Molecular nuclear fields: A naïve perspective

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A Gaussian function superposition is described in order to substitute the usual point charge approximation in molecular fixed frames. This procedure avoids the discontinuities at the nuclear positions which haunt first order density and EMP. Total first order density, made of the electronic and the Gaussian nuclear charge distributions, can be used to compute and compare molecular fields within quantum similarity techniques.

KEY WORDS: Nuclear repulsion field, density function, electrostatic molecular potential, molecular quantum similarity measures

1. Introduction

It has been already commented that the introduction of the nuclear field part, using the classical nuclear point charge framework in both density and EMP, now in other kind of molecular fields as these described so far here, provides with both type of functions, which are not suitable for general purposes as they offer discontinuities at the nuclei positions. Several years ago the author proposed a solution for this problem in EMP comparisons for quantum similarity purposes [1].

2. Taking into account the nuclear charges in one electron density

Here a simple possibility is proposed, consisting into associating at each nucleus not a point-like superposition of Dirac distributions but a Gaussian one, for instance writing the nuclear charge density of a given molecule with a fixed nuclear coordinate set $\mathbf{R}_F = \{\mathbf{R}_{F,I}\}$, as:

$$\rho_F^v(\mathbf{r} | \mathbf{R}_F) = \sum_{I \in F} Z_I \left[N(Z_I) \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F,I}|^2\right) \right],$$

where the explicit Gaussian functions for each nucleus are normalized in the Minkowski sense:

$$N(Z_I) \int_D \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F;I}|^2\right) d\mathbf{r} = 1$$

and $\theta(Z_I)$ is a function of the nuclear charge.

In this sense, one will have the Minkowski norm of the nuclear density function equal to the total charge of the molecular nuclei:

$$\int_D \rho_F^v(\mathbf{r} | \mathbf{R}_F) d\mathbf{r} = \sum_{I \in F} Z_I \left[N(Z_I) \int_D \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F;I}|^2\right) d\mathbf{r} \right] = \sum_I Z_I$$

The value of the Minkowski norm for each Gaussian contribution could easily found to be:

$$N(Z_I) = \left(\frac{\theta(Z_I)}{\pi} \right)^{\frac{3}{2}}.$$

A possible choice, which can be obviously refined, for such a function, $\theta(Z_I)$, could be:

$$\theta(Z_I) = \alpha Z_I^{-1},$$

using the constant α as a damping parameter with dimensions of inverse squared length. This choice will be the same as to consider the nuclei density more extended around the atomic center, as greater is the nuclear charge. Such a supposition can be assumed without problems, if the damping constant keeps the mean radius of the attached nuclear charge sufficiently small.

The mean square radius can be computed easily too, just writing:

$$\langle \mathbf{r}^2 \rangle = N(Z_I) \int_D |\mathbf{r} - \mathbf{R}_{F;I}|^2 \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F;I}|^2\right) d\mathbf{r} = \frac{1}{2\theta(Z_I)};$$

then, using the above specific definition of the function $\theta(Z_I)$:

$$\langle \mathbf{r}^2 \rangle = \frac{Z_I}{2\alpha} \rightarrow \alpha = \frac{Z_I}{2\langle \mathbf{r}^2 \rangle},$$

which taking into account the estimate of the mean square atomic radius as: $\langle \mathbf{r}^2 \rangle \approx 10^{-30} \text{au}^2$, provides an estimate of the damping factor of: $\alpha \approx \frac{Z_I}{2} 10^{30} \text{au}^{-2}$.

Moreover, whatever the function $\theta(Z_I)$ for each nucleus becomes infinite, then the Gaussian nuclear charge distribution transforms into a Dirac's distribution. This can be written easily as:

$$\lim_{\forall Z_I \rightarrow \infty} \rho_F^v(\mathbf{r} | \mathbf{R}_F) = \sum_{I \in F} Z_I \delta(\mathbf{r} - \mathbf{R}_{F;I}).$$

Thus, calling:

$$\rho_{F,I}^v(\mathbf{r} \mid \mathbf{R}_{F,I}; Z_I) = N(Z_I) \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F,I}|^2\right), \quad (1)$$

then:

$$\rho_F^v(\mathbf{r} \mid \mathbf{R}_F) = \sum_{I \in F} Z_I \rho_{F,I}^v(\mathbf{r} \mid \mathbf{R}_{F,I}; Z_I)$$

are the nuclear densities of a given molecular structure, therefore the total density can be written as:

$$\rho_F^T(\mathbf{r} \mid \mathbf{R}_F) = -\rho_F^\varepsilon(\mathbf{r} \mid \mathbf{R}_F) + \rho_F^v(\mathbf{r} \mid \mathbf{R}_F),$$

in such a way that the Minkowski norm of the total density becomes null in neutral molecules:

$$\langle \rho_F^T(\mathbf{r} \mid \mathbf{R}_F) \rangle = 0.$$

Such an arrangement can permit to use the total density within an integral without discontinuity problems.

3. Analysis of the nuclear density function

To the modified nuclear density function $\rho_F^v(\mathbf{r} \mid \mathbf{R}_F)$ one can apply the same analysis as Bader performed in the usual electronic density function [2]. Thus, the gradient can be written easily, if it is explicitly known the gradient and Hessian of a Gaussian function, like the one described in the equation (1). In the present case, this is trivial, as one can write both first and second derivatives without effort. A similar analysis has been performed on the ASA density functions recently [3] and as both approaches are formally the same, this subject will not be further commented.

4. Effect of the Gaussian nuclear charge distribution in the EMP

It has been discussed how the GNCD can be added to the density function without divergence problems when the total density is integrated in the Minkowski sense. How this will affect the definition of other molecular fields as EMP? The answer to this question will be discussed here.

The nuclear contribution using the Gaussian distribution so far described will have the form:

$$\begin{aligned} V_{N;F}(\mathbf{R}) &= \int_D |\mathbf{r} - \mathbf{R}|^{-1} \rho_F^v(\mathbf{r} | \mathbf{R}_F) d\mathbf{r} \\ &= \sum_{I \in F} Z_I \left[N(Z_I) \int_D |\mathbf{r} - \mathbf{R}|^{-1} \exp\left(-\theta(Z_I) |\mathbf{r} - \mathbf{R}_{F;I}|^2\right) d\mathbf{r} \right] \\ &= \sum_I Z_I V_{N;F,I}(Z_I; \mathbf{R}_{F;I} | \mathbf{R}) \end{aligned}$$

where the necessary integrals are well-known functions of the incomplete gamma function [4]:

$$V_{N;F,I}(Z_I; \mathbf{R}_{F;I} | \mathbf{R}) = 2 \left(\frac{\theta(Z_I)}{\pi} \right)^{\frac{1}{2}} F_0\left(\theta(Z_I) |\mathbf{R} - \mathbf{R}_{F;I}|^2\right).$$

5. Effect of a nuclear Gaussian charge distribution in quantum similarity comparisons of molecular fields

When two or more molecular fields are to be compared in the way density functions have been compared within quantum similarity measures, integrals of several kinds shall be taken into account. This section will be devoted to describe formally their structure.

5.1. Density quantum similarity comparison

Suppose two densities attached to two molecular structures F and M , which are composed by an electronic and a nuclear part each one, for example:

$$\rho_F(\mathbf{R}_F | \mathbf{R}) = -\rho_F^e(\mathbf{R}_F | \mathbf{R}) + \rho_F^v(\mathbf{R}_F | \mathbf{R}),$$

where \mathbf{R}_F represent the atomic coordinates of molecule F , while the same applies for molecule M .

Thus, four different kinds of contributions have to be taken into account when one tries to compare both densities by means of quantum similarity integral [5] weighted by some operator Ω :

$$\begin{aligned} Z_{FM}^{\kappa\lambda}(\Omega | \mathbf{R}_F; \mathbf{R}_M) \\ = \int_{\Delta'} \int_{\Delta} \rho_F^{\kappa}(\mathbf{R} | \mathbf{R}_F) \Omega(\mathbf{R}, \mathbf{R}') \rho_M^{\lambda}(\mathbf{R}' | \mathbf{R}_M) d\mathbf{R} d\mathbf{R}' \end{aligned} \quad (2)$$

where the subindices κ, λ can be associated to the electronic and nuclear contributions of the density, thus:

$$Z_{FM}(\Omega | \mathbf{R}_F; \mathbf{R}_M) = Z_{FM}^{\varepsilon\varepsilon} + Z_{FM}^{\nu\nu} - (Z_{FM}^{\varepsilon\nu} + Z_{FM}^{\nu\varepsilon}) \quad (3)$$

and on the right side of the equation the explicit operator and system coordinates have been avoided for easier description.

In this case, the operator Ω can be taken with arbitrary sign definition as the quantum similarity integrals $Z_{FM}(\Omega | \mathbf{R}_F; \mathbf{R}_M)$ are not necessarily positive definite due to the presence of the negative crossed terms in the integral of definition (3).

5.2. EMP quantum similarity comparison

The same contributions can be foreseen to appear when EMP or any other molecular field is taken into account. The case of EMP is important as it has been used in several quantum similarity studies in a manner where the discontinuities of the classical EMP form were not avoided [6]. The equivalent quantum similarity integral to the present definition (2), involving EMP, is slightly different:

$$\begin{aligned} Z_{FM}^{\kappa\lambda} &= \int_{\Delta'} \int_{\Delta} V_F^{\kappa}(\mathbf{R}) \Omega(\mathbf{R}, \mathbf{R}') V_M^{\lambda}(\mathbf{R}') d\mathbf{R} d\mathbf{R}' \\ &= \int_{\Delta'} \int_{\Delta} \left(\int_D \rho_F^{\kappa}(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} d\mathbf{r} \right) \Omega(\mathbf{R}, \mathbf{R}') \left(\int_{D'} \rho_M^{\lambda}(\mathbf{r}') |\mathbf{r}' - \mathbf{R}'|^{-1} d\mathbf{r}' \right) d\mathbf{R} d\mathbf{R}' \end{aligned}$$

The expression can be simplified choosing the operator as a Dirac delta function:

$$\Omega(\mathbf{R}, \mathbf{R}') = \delta(\mathbf{R} - \mathbf{R}'),$$

then one can write:

$$\begin{aligned} Z_{FM}^{\kappa\lambda} &= \int_{\Delta} \left(\int_D \rho_F^{\kappa}(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} d\mathbf{r} \right) \left(\int_{D'} \rho_M^{\lambda}(\mathbf{r}') |\mathbf{r}' - \mathbf{R}|^{-1} d\mathbf{r}' \right) d\mathbf{R} \\ &= \int_{\Delta} \int_{D'} \int_D \rho_F^{\kappa}(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} |\mathbf{r}' - \mathbf{R}|^{-1} \rho_M^{\lambda}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' d\mathbf{R} \end{aligned}$$

A simplification of the four contributing integrals can be envisaged using the alternative integration:

$$Z_{FM}^{\kappa\lambda} \approx \int_D \int_{D'} \rho_F^{\kappa}(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|^{-2} \rho_M^{\lambda}(\mathbf{r}') d\mathbf{r}' d\mathbf{r},$$

which has been described in a previous work [7].

6. Conclusions

A simple procedure to avoid discontinuities in the molecular field descriptors has been described. The form of the nuclear charge is constructed as a superposition of Gaussian functions normalized as to integrate to the sum of nuclear charges in a given molecule. A limit of the approximation provides the usual point-charge atomic model, as Gaussian functions become Dirac delta functions when the Gaussian exponent becomes infinite. The Gaussian nuclear charge distribution can be, thus, employed in describing total, that is: electronic plus nuclear contributions, molecular fields as first order density and EMP, without suffering of the problem of discontinuities when, for instance, they should be integrated. They can be employed as well in quantum similarity comparisons of molecular fields without more problems than the evaluation of the corresponding integrals involving Hermitian operators and products of Gaussian functions.

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