ORIGINAL PAPER

Coulomb repulsion, point-like nuclear charges, Dirac paradox, soft nuclear charge density and hypermultiplet nuclear repulsion

Ramon Carbó-Dorca

Abstract A discussion about the classical Coulomb repulsion via point-like nuclear charges, usually employed within Born–Oppenheimer approximation, leads to the description of Dirac paradox: an inconsistency found when describing nuclear charges by means of Dirac's distributions and computing with them nuclear Coulomb repulsion integrals. The way of overcoming Dirac paradox is bound to the description of soft Gaussian nuclear charge density and also to adopting a nuclear hypermultiplet Coulomb repulsion formulation. Such theoretical prospect produces a quantum mechanically compliant but simple algorithm in order to compute nuclear repulsion, which also appears to be consistently related to classical Coulomb repulsion energy, while avoiding singularities when nuclei collapse.

Keywords Point-like nuclear charges · Molecular Coulomb classical nuclear repulsion · Soft Gaussian nuclear charge density · Dirac paradox · Hypermultiplet quantum mechanical nuclear Coulomb repulsion

1 Introduction

Coulomb nuclear repulsion and Born–Oppenheimer approximation When generally describing any molecule in classical quantum chemistry under the Born–Oppenheimer approximation [1] and also in current molecular mechanics, nuclei are considered as a set of point-like positive charges, distributed in some frozen configuration in three dimensional (3D) space.

R. Carbó-Dorca (✉)
Facultat de Ciències, Institut de Química Computacional i Catàlisi, Universitat de Girona, 17071 Girona, Catalonia, Spain
e-mail: quantumqsar@hotmail.com; ramoncarbodorca@gmail.com

In order to discuss some way to complement the study of molecular structures, suppose that a set of N atoms is known, their associated atomic charges forming the set of positive numbers: $\mathbf{Z} = \{Z_I \,|\, I = 1, N\}$ and finally the configuration centers where the nuclei are placed in 3D space might be represented by the set of 3D real vectors: $\mathbf{C} = \{\mathbf{R}_I \,|\, I = 1, N\} \subset R^3$.

Then, the attached Coulomb repulsion is customarily computed in terms of the interatomic distances matrix, $\mathbf{D} = \{R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J| \,|\, I, J = 1, N\}$, as:

$$E_C = \frac{1}{2} \sum_I \sum_J \delta\,[I \neq J] \frac{Z_I Z_J}{R_{IJ}} \tag{1}$$

and added to the electronic energy to obtain the molecular internal energy. In Eq. (1) use is made of a logical Kronecker's delta, $\delta\,[L]$, where L is a logical expression which is subject to the convention: $\delta\,[.T.] = 1 \wedge \delta\,[.F.] = 0$.

The mainstream of quantum chemical molecular calculations systematically employs the classical point-like nuclear charges equation (1) to compute nuclear repulsion and to obtain in this way the total molecular energy.

It is curious to note now the obvious fact that nowadays one is facing quite sophisticated procedures to solve Schrödinger equation, while at the end of the computational process appears that it is added to the quantum mechanical electronic energy result, a trivial classically bound nuclear term like the one in Eq. (1). Thus, there seems interesting and reasonable to try refining such a simple nuclear repulsion algorithm, attempting to transform it into a similar one, but formulated within a more adequate quantum mechanical formalism.

2 Dirac nuclear charge density distribution

A reflection over the usual point-like Coulomb repulsion, which is systematically used when molecular total energies are computed, might lead first to the proposal of a nuclear charge density, which can be provisionally based on Dirac 3D distributions centered at each nucleus:

$$\forall I = 1, N : \sigma_I(\mathbf{R}) = \delta(\mathbf{R} - \mathbf{R}_I) \rightarrow \langle \sigma_I \rangle = \int_{-\infty}^{+\infty} \delta(\mathbf{R} - \mathbf{R}_I)\, d\mathbf{R} = 1 \tag{2}$$

Such nuclear functions can be considered as nuclear shape functions and can be easily transformed into nuclear charge densities, just scaling them by the atomic numbers:

$$\forall I = 1, N : \rho_I^D(\mathbf{R}) = Z_I \sigma_I(\mathbf{R}). \tag{3}$$

Summing up the nuclear charge densities described in this way, a total Dirac nuclear charge density $\rho_D(\mathbf{R})$ like:

$$\rho_D(\mathbf{R}) = \sum_I \rho_I^D(\mathbf{R}) = \sum_I Z_I \sigma_I(\mathbf{R}) \tag{4}$$

can be constructed for any molecule in any conformation. The Minkowski norm of the Dirac nuclear charge density as constructed in Eq. (4) provides the total number of charges v contained into the molecule:

$$\int_V \rho_D (\mathbf{R}) \, d\mathbf{R} = \langle \rho_D \rangle = \sum_I Z_I \langle \sigma_I \rangle = \sum_I Z_I = v.$$

The continuous Dirac nuclear density function as described above, which apparently provides a quantum approximation to the nuclear charge distribution in any molecular conformation, can be added to the usual quantum mechanical electronic density: $\rho_e (\mathbf{r})$, yielding a total molecular charge density function, which might be written as:

$$\rho (\mathbf{r}, \mathbf{R}) = \rho_e (\mathbf{r}) + \rho_D (\mathbf{R}) . \tag{5}$$

3 Dirac's paradox

However, proceeding in this way to obtain a formal quantum mechanical global charge density (5), a puzzling situation is encountered when trying to use the nuclear charge density, by means of nuclear Dirac distributions: $\rho_D (\mathbf{R})$, as defined in Eq. (4), when computing any Coulomb nuclear repulsion calculation.

The anomaly which can be named *Dirac's Paradox* appears when a smooth continuous density function is built up as in Eq. (4), via a superposition of Dirac nuclear charge distributions defined as in (3). Such Dirac nuclear density can be furthermore used to compute the Coulomb repulsion using an appropriate electrostatic interaction integral:

$$E_D = \int_V \int_V \rho_D (\mathbf{R}') \rho_D (\mathbf{R}'') \left| \mathbf{R}' - \mathbf{R}'' \right|^{-1} d\mathbf{R}' d\mathbf{R}''. \tag{6}$$

Substitution of the nuclear density (4) into the integral (6) trivially leads to an expression formed by a double sum of diatomic terms, which can be written as:

$$E_D = \sum_I \sum_J Z_I Z_J \int_V \int_V \sigma_I (\mathbf{R}') \sigma_J (\mathbf{R}'') \left| \mathbf{R}' - \mathbf{R}'' \right|^{-1} d\mathbf{R}' d\mathbf{R}'' \tag{7}$$

and these diatomic integrals, when two atoms are not coincident, produce the associated point-like Coulomb repulsion terms written as in Eq. (1):

$$\forall I, J : Z_I Z_J \int_V \int_V \sigma_I (\mathbf{R}') \sigma_J (\mathbf{R}'') \left| \mathbf{R}' - \mathbf{R}'' \right|^{-1} d\mathbf{R}' d\mathbf{R}''$$
$$= Z_I Z_J \int_V \int_V \delta (\mathbf{R}' - \mathbf{R}_I) \delta (\mathbf{R}'' - \mathbf{R}_J) \left| \mathbf{R}' - \mathbf{R}'' \right|^{-1} d\mathbf{R}' d\mathbf{R}''$$
$$= Z_I Z_J \left| \mathbf{R}_I - \mathbf{R}_J \right|^{-1}$$

However, proceeding in this way, a set of selfrepulsion contributions appear, which produce a set of infinity values. As many as atoms included within the molecular frame, because in the diagonal of the summations in Eq. (7) one will necessarily find:

$$\forall I = 1, N : Z_I^2 \left| \mathbf{R}_I - \mathbf{R}_I \right|^{-1} . \tag{8}$$

Therefore, a nuclear continuous density function, which apparently corresponds to a point-like atomic charge distribution as in Eq. (4), can be easily constructed. However, within the corresponding continuous electrostatic context, its use produces in the double summation of Eq. (7) the appearance of divergent diagonal terms. As an extra problem appearing in addition, a double contribution of the off-diagonal elements is also included in the Eq. (7).

Evidently, a correct version of Eq. (7) can be described, just modifying the resultant electrostatic expression, which could be formally transformed into a similar structure as the one in Eq. (1), which can be written as:

$$E_C = \frac{1}{2} \sum_I \sum_J \delta \left[I \neq J \right] Z_I Z_J \int_V \int_V \sigma_I \left(\mathbf{R}' \right) \sigma_J \left(\mathbf{R}'' \right) \left| \mathbf{R}' - \mathbf{R}'' \right|^{-1} d\mathbf{R}' d\mathbf{R}''. \tag{9}$$

Nonetheless, even if the correct point-like Coulomb form (1) is recovered, one must be aware that there is present some inconsistency derived from Eq. (6), which must be corrected transforming it as Eq. (9). Then, after this *a posteriori* handling, both Eqs. (1) and (9) become the same.

In the author's opinion, such inconsistent scenery provides the logical structure of *Dirac's Paradox*, which can be more precisely stated as follows. Whenever a set of point-like charges arbitrarily situated in 3D space and, in order to obtain a quantum mechanical adequate description of the nuclear charge distribution, then when it is represented by a continuous charge density distribution, using a superposition of Dirac's functions, at this moment some anomalies appear in the Coulomb expression of the electrostatic repulsion. Such inconsistency can be avoided manipulating afterwards the resultant electrostatic expression accordingly.

Thus, it seems interesting that some research can be performed, just to obtain an expression for the nuclear density and the implicit electrostatic repulsion, which overcomes Dirac's paradox. The present study will try to find out one plausible way to accomplish this viewpoint.

4 Soft Gaussian nuclear density

While classical quantum chemistry keeps considering nuclear charges as point-like, in relativistic quantum chemistry the use of finite nuclear structures is widespread, as the encyclopedic work of Andrae [2] shows. What follows has been inspired by one of the multiple options which the work of Andrae describes.

Attempting the resolution of Dirac's paradox, has lead first to the definition of a soft Gaussian nuclear charge distribution, then to the construction of a Coulomb nuclear repulsion in several previous papers [8–10]. Such new nuclear density function avoids the typical divergences, encountered when two nuclei coincide in the same point of 3D space. However, the final result still contains terms of selfrepulsion, which have not an obvious theoretical explanation. All these issues will be discussed below.

For a given molecule with a set of fixed coordinates, one can write the atomic positions in a general way with a real 3D vector set like: $\mathbf{C} = \{\mathbf{R}_I \,|\, I = 1, N\} \subset R^3$, as constructed at the beginning. Then, at each nucleus can be centered a Minkowski normalized Gaussian function, which can be defined as follows:

$$\forall I = 1, N : \gamma_I(\mathbf{R}) = \gamma(\theta \,|\mathbf{R} - \mathbf{R}_I|) = \left(\frac{\theta}{\pi}\right)^{\frac{3}{2}} \exp\left(-\theta \,|\mathbf{R} - \mathbf{R}_I|^2\right),$$

$$\rightarrow \langle \gamma_I \rangle = \int_V \gamma(\theta \,|\mathbf{R} - \mathbf{R}_I|)\, d\mathbf{R} = 1 \tag{10}$$

where θ is an appropriate exponent for the nuclear Gaussian charge distribution, which can be assumed equivalent for any nucleus. Such a set of functions can be considered as a *soft* nuclear shape function set. In contrast of the Dirac's shape functions described in Eq. (2), which could be named as *sharp* nuclear charge distributions. Multiplying each Gaussian shape function by the nuclear charge yields the set of soft Gaussian nuclear charge densities:

$$\forall I = 1, N : \rho_I^S(\mathbf{R}) = Z_I \gamma(\theta \,|\mathbf{R} - \mathbf{R}_I|).$$

The superposition of these charge densities can be used to construct the total soft Gaussian nuclear charge density:

$$\rho_S(\mathbf{R}) = \sum_I \rho_I^S(\mathbf{R}) = \sum_I Z_I \gamma(\theta \,|\mathbf{R} - \mathbf{R}_I|) = \sum_I Z_I \gamma_I(\mathbf{R}), \tag{11}$$

The total soft Gaussian nuclear density constitutes a simple expression, which can be also seen as a linear combination referred to a set of Gaussian space enfoldment points [3,4]. On the other hand, such a nuclear soft density representation is directly related with the so-called promolecular electronic density and the ASA [5–7] simplified representation of the molecular electronic density functions.

The above expression (11) possesses a Minkowski norm equal to the number of charges v contained into the considered molecule, in the same way as Dirac nuclear density defined in Eq. (4), that is:

$$\langle \rho_S \rangle = \sum_I \left\langle \rho_I^S \right\rangle = \sum_I Z_I \langle \gamma_I \rangle = \sum_I Z_I = v.$$

Moreover, due to the property of Gaussian functions to transform into a Dirac distribution when the exponent becomes infinity, that is:

$$\lim_{\theta \to \infty} \gamma(\theta \,|\mathbf{R} - \mathbf{R}_I|) = \delta(\mathbf{R} - \mathbf{R}_I),$$

then one can easily deduce that the soft Gaussian nuclear density transforms into a Dirac nuclear density in the same manner:

$$\lim_{\theta \to \infty} \rho_S(\mathbf{R}) = \rho_D(\mathbf{R}).$$

Therefore, choosing the total soft Gaussian nuclear charge density written as in Eq. (11), the limit of the exponent when it goes to infinity is the Dirac nuclear density as described in Eq. (4).

5 Soft Coulomb nuclear repulsion energy

The possible expression of the nuclear repulsion by means of Dirac distributions of nuclear charges and the attached paradox previously discussed, leads to consider the transformation of the terms of Eq. (6) into a general but more flexible formulation devoid of paradoxes.

This construct is such that it might be called: *soft* nuclear repulsion electrostatic energy. In a similar way as it has been recently proposed for the definition of soft electrostatic molecular potentials (SEMP) [8,9] and described in a general molecular context [10]. In this general but malleable framework, the divergent terms present as Eq. (8) shows, they could be transformed into conformationally invariant finite constants, thus solving in this manner the nuclear repulsion Dirac paradox, but adding the necessity of interpret the meaning of such a constant presence in soft nuclear repulsion expressions.

Generalizing a previous result on atoms by Weinstein et al. [11], recently it has been shown that the electronic MEP, generated by an electronic density written similarly as Eq. (11), in the framework of polyatomic molecules, becomes everywhere positive [8]. Despite of this drawback, the electronic MEP generated by both a polarized ASA density and a soft nuclear potential preserves the classical MEP structure, while eliminating the atomic infinities [9] of the classical customary calculations. Obviously enough, in the present case of soft Gaussian nuclear densities it is not a drawback to realize that the soft Gaussian nuclear charge distribution and a possible potential generated by it is everywhere positive, as one is trying to describe the positive nuclear charge distribution.

Dirac's delta functions can be considered the limit of some Minkowski normalized Gaussian function, as it has been commented beforehand, then, after considering this straightforward development, the soft nuclear repulsion energy for any molecule can be proposed to be evaluated with the following expression, equivalent to Eq. (6):

$$E_S = \int_V \int_V \rho_S\left(\mathbf{R}'\right) \rho_S\left(\mathbf{R}''\right) \left|\mathbf{R}' - \mathbf{R}''\right|^{-1} d\mathbf{R}' d\mathbf{R}''$$

and after taking into account the definition of the soft Gaussian nuclear density as written in Eq. (11) it can be also written:

$$E_S = \sum_I \sum_J Z_I Z_J \int_D \int_D \left|\mathbf{R}' - \mathbf{R}''\right|^{-1} \gamma\left(\theta \,\middle|\, \mathbf{R}' - \mathbf{R}_I\right) \gamma\left(\theta \,\middle|\, \mathbf{R}'' - \mathbf{R}_J\right) d\mathbf{R}' d\mathbf{R}''.$$

$$(12)$$

6 Incomplete gamma and error functions expression of the soft Gaussian nuclear repulsion terms

The two atom contribution terms formed by integrals scaled by the nuclear charges found in Eq. (12), can be easily obtained as functions of the internuclear distances: $\mathbf{D} = \{R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J| \,|\, I, J = 1, N\}$.

6.1 Incomplete gamma function expression

For example, through Saunders exhaustive description [12] of Gaussian function molecular integrals, they can be easily written as:

$$\forall I, J = 1, N : E_{IJ}^S (R_{IJ}) = 2Z_I Z_J \left(\frac{\theta}{2\pi}\right)^{\frac{1}{2}} F_0 \left(\frac{\theta}{2} R_{IJ}^2\right), \tag{13}$$

where $F_0(x)$ corresponds to the zeroth order incomplete gamma function.

Equation (12) will be indeed everywhere positive, but contrarily to the usual nuclear repulsion energy, do not possess singularity values when nuclei collapse and coincide in space, because $F_0(0) = 1$, and therefore:

$$\forall I = 1, N : E_{II}^S (0) = 2Z_I^2 \left(\frac{\theta}{2\pi}\right)^{\frac{1}{2}}.$$

Such a feature is quite interesting to be taken into account, when considering the systematic generation of molecular total potential energy surfaces in any kind of automatic computational structure.

6.2 Error function expression

The resultant soft nuclear repulsion energy can be also equivalently written in terms of the error function. As the incomplete gamma function and the error function are related by means of the following equality [12]:

$$F_0(x) = \int_0^1 e^{-xt^2} dt = \frac{1}{2}\sqrt{\frac{\pi}{x}} erf\left(\sqrt{x}\right),$$

then, the soft nuclear repulsion term as expressed in Eq. (13) can be also alternatively written by means of the error function:

$$\forall I, \quad J = 1, \quad N : E_{IJ}^S = \frac{Z_I Z_J}{R_{IJ}} erf\left(\left(\frac{\theta}{2}\right)^{\frac{1}{2}} R_{IJ}\right).$$

Expressed in this way, the soft nuclear repulsion terms can be easily interpreted as a classical point-like Coulomb element: $Z_I Z_J R_{IJ}^{-1}$, weighted by the error function

term. Because the error function values belong to the unit interval: [0, 1], then the soft nuclear repulsion term can be observed as a Coulomb element, which can be less repulsive than the classical one, the percentage difference ratio being related to the error function.

7 Hypermultiplet form of the soft repulsion energy

Next, in order to refine the Coulomb repulsion model based on soft Gaussian nuclear charge density, one can inspect the electronic repulsion part in hypermultiplet cases, as defined in reference [14], that is: the repulsion energy expression in sets of particles with spin, where all the spins are not coupled. The particle set can be described by means of a wave function made by a unique Slater determinant with all the particles being chosen with alpha or beta spin functions. In fact, this situation also reminds of the theory of ferromagnetism described by Heisenberg [15], which has been set up in the early stages of quantum mechanics development, provided here as an old previous example of such a possible similar situation with a set of several nuclei.

The resulting electronic repulsion energy expression for hypermultiplets in MO theory can be written easily as [14]:

$$E_R = \frac{1}{2} \sum_P \sum_Q \left(J_{PQ} - K_{PQ} \right) \qquad (14)$$

where the sums run over all the singly occupied MO's and $\{J_{PQ}\}, \{K_{PQ}\}$ correspond to the Coulomb and exchange integrals, see for example reference [16], computed over the MO set. Expression (14) can be written by means of the hypermultiplet electronic density defined as a superposition over a real MO density set: $\{\rho_{PQ}\left(\mathbf{r}', \mathbf{r}''\right) = \psi_P\left(\mathbf{r}'\right)\psi_Q\left(\mathbf{r}''\right) | P, Q = 1, M\}$:

$$\rho_e\left(\mathbf{r}\right) = \rho_e\left(\mathbf{r}, \mathbf{r}\right) = \sum_P \rho_{PP}\left(\mathbf{r}, \mathbf{r}\right) = \sum_P |\psi_P\left(\mathbf{r}\right)|^2$$

and the electronic repulsion can be described by means of the integrals:

$$E_R = \frac{1}{2} \sum_P \sum_Q \left(\left\langle \rho_{PP}\left(\mathbf{r}', \mathbf{r}'\right) |\mathbf{r}' - \mathbf{r}''|^{-1} \rho_{QQ}\left(\mathbf{r}'', \mathbf{r}''\right) \right\rangle \right.$$
$$\left. - \left\langle \rho_{PQ}\left(\mathbf{r}', \mathbf{r}''\right) |\mathbf{r}' - \mathbf{r}''|^{-1} \rho_{PQ}\left(\mathbf{r}', \mathbf{r}''\right) \right\rangle \right).$$

Equation (14) permits to reconsider the calculation of the nuclear repulsion based in soft Gaussian nuclear density in a similar way. Using these considerations, then a final expression of the soft nuclear repulsion can be set up, where the final equation appearance appears devoid of paradoxes, selfrepulsion terms are avoided and therefore singularities at atomic collapse are entirely circumvented.

Using the Minkowski normalized Gaussian function, as already described in Eq. (10), it is easy to realize that it can be rewritten in terms of the normalization factor by the Gaussian function itself:

$$\gamma\left(\theta\,|\mathbf{R}-\mathbf{R}_I\right) = \left(\frac{\theta}{\pi}\right)^{\frac{3}{2}} \exp\left(-\theta\,|\mathbf{R}-\mathbf{R}_I|^2\right)$$

$$= \left(\frac{\theta}{\pi}\right)^{\frac{3}{2}} g\left(\theta\,|\mathbf{R}-\mathbf{R}_I\right) = M\left(\theta\right) g\left(\theta\,|\mathbf{R}-\mathbf{R}_I\right)$$

Then one can suppose that the Coulomb expression of nuclear repulsion will have an exchange term, like in the hypermultiplet molecular electronic part of Eq. (14). So, each repulsion pair contribution could be written using a mixed Gaussian term. That is, defining the Coulomb part as the integral, where the Minkowski norm squared appears to be a global scale factor:

$$E_{IJ}^C = (II\,|JJ)$$
$$= Z_I Z_J M^2\left(\theta\right)\left[\int_D \int_D |\mathbf{R}'-\mathbf{R}''|^{-1} g\left(\theta|\,\mathbf{R}'-\mathbf{R}_I\right) g\left(\theta|\,\mathbf{R}''-\mathbf{R}_J\right) d\mathbf{R}'d\mathbf{R}''\right]$$

This is the same in fact as Eq. (13), thus it can be written:

$$\forall I, J = 1, N : E_{IJ}^C\left(R_{IJ}\right) = 2Z_I Z_J \left(\frac{\theta}{2\pi}\right)^{\frac{1}{2}} F_0\left(\frac{\theta}{2} R_{IJ}^2\right)$$

To obtain the exchange terms one can start taking into account now that any Gaussian function can be easily written as a split product:

$$\exp\left(-\theta\,|\mathbf{R}-\mathbf{R}_I|^2\right) = \exp\left(-\frac{\theta}{2}\,|\mathbf{R}-\mathbf{R}_I|^2\right)\exp\left(-\frac{\theta}{2}\,|\mathbf{R}-\mathbf{R}_I|^2\right)$$

This simple property can be also used to write an exchange of the charge variable in the following way:

$$G\left(\frac{\theta}{2}\middle|\mathbf{R}';\mathbf{R}_I;\mathbf{R}_J\right) = g\left(\frac{\theta}{2}\middle|\mathbf{R}'-\mathbf{R}_I\right) g\left(\frac{\theta}{2}\middle|\mathbf{R}'-\mathbf{R}_J\right)$$

and

$$G\left(\frac{\theta}{2}\middle|\mathbf{R}'';\mathbf{R}_I;\mathbf{R}_J\right) = g\left(\frac{\theta}{2}\middle|\mathbf{R}''-\mathbf{R}_I\right) g\left(\frac{\theta}{2}\middle|\mathbf{R}''-\mathbf{R}_J\right)$$

But taking into account that when: $\mathbf{R}_I = \mathbf{R}_J$ then the double centered functions become the original one. For example:

$$G\left(\frac{\theta}{2}\middle|\mathbf{R}';\mathbf{R}_I;\mathbf{R}_I\right) = g\left(\theta|\,\mathbf{R}'-\mathbf{R}_I\right) \wedge G\left(\frac{\theta}{2}\middle|\mathbf{R}'';\mathbf{R}_J;\mathbf{R}_J\right) = g\left(\theta|\,\mathbf{R}''-\mathbf{R}_J\right),$$

then it can be also written an exchange term as:

$$
\begin{aligned}
E_{IJ}^{E} &= (IJ \,|\, IJ) \\
&= Z_I Z_J M^2 (\theta) \left[\int_D \int_D |\mathbf{R}' - \mathbf{R}''|^{-1} G\left(\frac{\theta}{2} \middle| \mathbf{R}'; \mathbf{R}_I; \mathbf{R}_J \right) \right. \\
&\quad \left. \times \, G\left(\frac{\theta}{2} \middle| \mathbf{R}''; \mathbf{R}_I; \mathbf{R}_J \right) d\mathbf{R}' d\mathbf{R}'' \right]
\end{aligned}
$$

When looking for the monocentric contributions, that is when $I = J$, then the difference between both integral contributions will become null, as the following equality holds:

$$
\int_D \int_D |\mathbf{R}' - \mathbf{R}''|^{-1} G\left(\frac{\theta}{2} \middle| \mathbf{R}'; \mathbf{R}_I; \mathbf{R}_I \right) G\left(\frac{\theta}{2} \middle| \mathbf{R}''; \mathbf{R}_I; \mathbf{R}_I \right) d\mathbf{R}' d\mathbf{R}''
$$

$$
= \int_D \int_D |\mathbf{R}' - \mathbf{R}''|^{-1} \gamma \left(\theta | \mathbf{R}' - \mathbf{R}_I \right) \gamma \left(\theta | \mathbf{R}'' - \mathbf{R}_I \right) d\mathbf{R}' d\mathbf{R}''
$$

So, the selfrepulsion terms will be null and do not contribute to the repulsion energy in this nuclear hypermultiplet framework. As the product of two Gaussian functions centered at two different sites is another function centered in this case at the midpoint, one can write in general:

$$
\begin{aligned}
G\left(\frac{\theta}{2} \middle| \mathbf{R}'; \mathbf{R}_I; \mathbf{R}_J \right) &= g\left(\frac{\theta}{2} \middle| \mathbf{R}' - \mathbf{R}_I \right) g\left(\frac{\theta}{2} \middle| \mathbf{R}' - \mathbf{R}_J \right) \\
&= \exp\left(-\frac{\theta}{4} |\mathbf{R}_I - \mathbf{R}_J|^2 \right) g\left(\theta | \mathbf{R}' - \mathbf{P} \right) \leftarrow \mathbf{P} = \frac{1}{2} (\mathbf{R}_I + \mathbf{R}_J)
\end{aligned}
$$

Therefore, using the same transformation for the second charge coordinate, the exchange term can be written in fact as a monocentric Coulomb repulsion:

$$
\begin{aligned}
(IJ \,|\, IJ) &= Z_I Z_J M^2 (\theta) \exp\left(-\frac{\theta}{2} |\mathbf{R}_I - \mathbf{R}_J|^2 \right) \\
&\quad \int_D \int_D |\mathbf{R}' - \mathbf{R}''|^{-1} g\left(\theta | \mathbf{R}' - \mathbf{P} \right) g\left(\theta | \mathbf{R}'' - \mathbf{P} \right) d\mathbf{R}' d\mathbf{R}'',
\end{aligned}
$$

which can be evaluated in a similar way as the Coulomb terms, see again reference [12], but taking into account that the integral is monocentric, yielding:

$$
\begin{aligned}
(IJ \,|\, IJ) &= Z_I Z_J \left(\frac{\theta}{\pi} \right)^3 \exp\left(-\frac{\theta}{2} |\mathbf{R}_I - \mathbf{R}_J|^2 \right) \frac{2\pi^{\frac{5}{2}}}{\theta^2 \sqrt{2\theta}} \\
&= Z_I Z_J \left(\frac{2\theta}{\pi} \right)^{\frac{1}{2}} \exp\left(-\frac{\theta}{2} |\mathbf{R}_I - \mathbf{R}_J|^2 \right) = Z_I Z_J \left(\frac{2\theta}{\pi} \right)^{\frac{1}{2}} \exp\left(-\frac{\theta R_{IJ}^2}{2} \right)
\end{aligned}
$$

Therefore, the final two center hypermultiplet nuclear repulsion terms can be written in terms of the incomplete gamma function as:

$$\forall I, J = 1, N : E_{IJ}^{H}(R_{IJ}) = Z_I Z_J \left(\frac{2\theta}{\pi}\right)^{\frac{1}{2}} \left[F_0 \left(\frac{\theta}{2} R_{IJ}^2\right) - \exp\left(-\frac{\theta R_{IJ}^2}{2}\right) \right]$$

where one can easily see that:

$$\forall I = 1, N : E_{II}^{H}(0) = 0.$$

Then, in fact, the hypermultiplet soft Gaussian nuclear repulsion can be written using the final expression:

$$E_H = \frac{1}{2} \sum_I \sum_J E_{IJ}^{H} = \frac{1}{2} \left(\frac{2\theta}{\pi}\right)^{\frac{1}{2}} \sum_I \sum_J Z_I Z_J \left[F_0 \left(\frac{\theta}{2} R_{IJ}^2\right) - \exp\left(-\frac{\theta R_{IJ}^2}{2}\right) \right].$$

(15)

Despite of the inclusion of diagonal terms, which now do not contribute due they are null, and although off-diagonal elements are twice repeated the whole formulation is naturally half scaled, therefore the above Eq. (15) is devoid of inconsistencies and completely equivalent to the simplified form, which appears without any manipulation to be also written as:

$$E_H = \sum_I \sum_J \delta\left[I < J\right] E_{IJ}^{H}.$$

In this sense, one can say that the use of Eq. (15) becomes equivalent to substituting the point-like charges of two distinct center Coulomb terms by the hypermultiplet repulsion ones:

$$\forall I = 1, N - 1 \wedge J = I + 1, N : \frac{Z_I Z_J}{R_{IJ}} \Rightarrow E_{IJ}^{H}.$$

Moreover, due to the existence of the recursive formula [12], see "Appendix", which relates incomplete gamma functions, it can be also possible to write equation (15) in terms of the incomplete gamma function of the first order:

$$E_H = \theta \left(\frac{\theta}{2\pi}\right)^{\frac{1}{2}} \sum_I \sum_J Z_I Z_J R_{IJ}^2 F_1 \left(\frac{\theta}{2} R_{IJ}^2\right).$$

8 Discussion of the results

It has been described first how the connection of classical Coulomb nuclear repulsion, associated to point-like charges, when compared with Dirac distributions of nuclear charges, which apparently must mimic the former repulsion formula, appears

providing inconsistent results. Dirac's nuclear density can be seen as a quantum mechanical continuous description of point-like nuclear charges, but if used into a Coulomb repulsion integral calculation, some anomalies result, which can be easily corrected *a posteriori* to provide the usual classical result. This situation has been named here the *Dirac paradox*. However, such a manipulation appears to be not completely satisfactory, even if providing an equivalent expression to the classical Coulomb one.

On the way to overcome Dirac's paradox, an idea, borrowed from relativistic quantum chemistry, has been employed. Such procedure has been previously tested to obtain molecular electrostatic potentials devoid of atomic singularities, providing satisfactory results. The procedure consists on substituting point-like nuclear charges by defining Gaussian nuclear charge distributions, or soft nuclear charge densities. Afterwards, a continuous molecular charge density from their superposition is straightforwardly constructed. In this way the nuclear singularities disappear from the Coulomb repulsion integral. Nevertheless, conformationally invariant terms, which present some need to be interpreted as positive zero global energy levels, do appear.

Because in the definition of soft Gaussian nuclear charge density still some inconsistency is present when Coulomb repulsion is evaluated, even if the proposed soft density appears more adequate to quantum mechanical description of nuclear charges, further thinking has been put forward in order to get rid of any problem.

In order to obtain a fully consistent description of Coulomb repulsion via a soft nuclear charge density, it has been further introduced a hypermultiplet Coulomb repulsion model of the nuclear spins. Such a model, which reminds of the Heisenberg ferromagnetism, can be easily attached to the individual Gaussian nuclear charge distributions. Providing in this manner an easily implemented computational structure, which is compliant to a quantum mechanical scope, producing a resultant nuclear Coulomb repulsion which has been taking into account nuclear spins, generating a result devoid of Dirac paradox and consistent with the classical nuclear Coulomb repulsion form.

Also, as one of the referees has pointed out, the theoretical foundations and the practical algorithms developed in this paper can be related first to the generalized DFT [18] framework, where nuclear point like charges appear not adequate, and second provide with a possible refinement of the conceptual DFT treatment of molecular electrostatic potentials [19,20], where the potential singularities have to be eliminated by hand.

Finally, at the light of the present theoretical development, related to the soft Coulomb nuclear repulsion and described in terms of a hypermultiplet energy expression, one might conclude that classical Coulomb repulsion perhaps can be observed as corresponding to some kind of simplified version of an involved quantum mechanical description of the repulsion energy, associated to nuclei forming molecular frames.

9 Appendix

9.1 Incomplete gamma function

A set of polynomial expressions to accurately compute the incomplete gamma functions needed here was published by Arents [17]. Also, knowing any higher order term, then a unit order inferior function can be easily obtained by means of the descending iteration [11]:

$$F_p(x) = \frac{1}{2p+1}\left(2x F_{p+1}(x) + e^{-x}\right)$$

Then, one can also write:

$$F_0\left(\frac{\theta}{2}R_{IJ}^2\right) - \exp\left(-\frac{\theta R_{IJ}^2}{2}\right) = \theta R_{IJ}^2 F_1\left(\frac{\theta}{2}R_{IJ}^2\right)$$

9.2 Derivatives

Derivatives of the incomplete gamma function and error function are not at all difficult to obtain. They can be useful for general geometry optimization purposes.

A of the incomplete gamma function

The derivatives of the incomplete gamma function of any order can be expressed [12] in terms of the incomplete gamma function of a unit superior order:

$$\frac{\partial F_p(x)}{\partial x} = -F_{p+1}(x).$$

B of the error function

Derivatives of the error function are readily computed in terms of Hermite polynomials [13]:

$$\forall n = 0, 1, 2, \ldots : \quad \frac{d^{n+1}}{dx^{n+1}} erf(x) = (-1)^n \frac{2}{\sqrt{\pi}} H_n(x) e^{-x^2}.$$

Thus, the first derivative term, owing to the fact that also: $H_0(x) = 1$ holds, corresponds to:

$$\frac{d}{dx} erf(x) = \frac{2}{\sqrt{\pi}} e^{-x^2}.$$

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