Soft nuclear density and nuclear repulsion

Ramon Carbó-Dorca
Institut de Química Computacional i Catàlisi, Universitat de Girona, Catalonia, Spain
Email: quantumqsar@hotmail.com

Received 2 April 2014; accepted 9 May 2014

This paper proposes the description of a soft nuclear density and the associated soft nuclear Coulombic repulsion. The idea just consists into describing soft nuclear repulsion expressions substituting the usual point-like nuclear charge density by means of a Gaussian distribution. The theoretical structure and management of such an approach is discussed.

Keywords: Theoretical chemistry, Born-Oppenheimer approximation, Nuclear density, Soft nuclear density, Nuclear repulsion, Soft nuclear repulsion

Point-like Coulomb Nuclear Repulsion Energy

In molecular calculations within Born-Oppenheimer approximation (BOA), the nuclear repulsion energy is added to the computed quantum mechanical electronic energy to obtain the total energy of the system. For long, the work of Woolley and Sutcliffe has been a continued analysis of the structure of the quantum chemical problems associated to BOA.

For a molecule with \( N \) atoms attached to a set of fixed coordinates, \( R = \{ R_i \}_{i=1}^N \), and with atomic numbers, \( Z = \{ Z_i \}_{i=1}^N \), the nuclear repulsion energy is classically written as the sum of Coulomb repulsion contributions (Eq. 1),

\[
E_N = \sum_{i<j} Z_i Z_j |R_i - R_j|^{-1} = \sum_{i<j} Z_i Z_j R_{ij}^{-1} = \sum_{i<j} E_{N,ij}
\]

(1)

where \( \{ R_{ij} \} \) is the set of interatomic distances. Equation (1) above is to be added to the electronic energy. It must be noted that Eq. (1) might be also included in empirical estimation of molecular energies by means of several contributions due to bond energy simulation, stretching, bending; see for example Ref. 6 and also the discussion in the final section.

This method is obviously equivalent to considering the nuclear positive charges as point-like, and also where the self-repulsion terms issuing from zero distances, \( \{ R_{ii} = 0 \} \), are eliminated. They are ignored for the obvious reason that including such self-repulsion terms will lead to Coulomb singularities, providing infinity divergence to Eq. (1). Therefore, in view of the above, one can say that the electronic energy is obtained via a BOA simplification, whereas the nuclear repulsion is found classically. There has not been any relevant objection to such a successful computational process, which mixes quantum mechanical results with classical electrostatic pictures.

Dirac’s Nuclear Charge Density Distributions

Yet, a point-like charge \( Z \) located to a space position \( R \) can be associated to a Dirac distribution, yielding a charge density distribution, which can be written as Eq. (2),

\[
P(r - R) = Z \delta(r - R)
\]

(2)

in such a way that the Minkowski norm of the distribution (2) will yield

\[
\langle P \rangle = Z \int_{\mathbb{R}^3} \delta(r - R) \, dr = Z
\]

Consequently, a molecular nuclear charge density distribution can be associated to a superposition of some set of Dirac distributions, constructed like Eq. (2) and centered at each atomic position. Then,

\[
\{ P_i (r - R_i) = Z_i \delta(r - R_i) | i = 1, N \}
\]

Thus, one can write a point-like molecular charge density function (DF), more suitable to obtain, if
possible, expectation values from the quantum mechanical viewpoint (Eq. 3).

\[ \rho_N (\mathbf{r}) = \sum_i P_i (\mathbf{r} - \mathbf{R}_i) = \sum_i Z_i \delta (\mathbf{r} - \mathbf{R}_i) \quad \ldots(3) \]

Such a resulting DF written as in Eq. (3) can be seen as a linear combination of Dirac distributions, whose coefficients coincide with the nuclear charges. Upon Minkowski norm evaluation, the function (3) in neutrally charged systems produces the molecular number of electrons \( v \),

\[ \langle \rho_N (\mathbf{r}) \rangle = \sum_{i=1}^{N} Z_i \langle \delta (\mathbf{r} - \mathbf{R}_i) \rangle = \sum_{i=1}^{N} Z_i = v \]

as in neutral atoms each nuclear charge equals the number of electrons. Once defined the nuclear charge distribution (3), then expression (1) can be apparently written as an equivalent continuous electrostatic repulsion energy expression,

\[ E_N = \frac{1}{2} \sum_i \sum_{J \neq i} \delta [I \neq J] E_{N,II} \]

using a logical Kronecker delta symbol: \( \delta [I \neq J] \), which will become one if \( I \neq J \) and zero if \( I = J \), thus obviating the inclusion of the infinite self-repulsion.

**Soft Nuclear Density**

Suppose again a molecular structure with \( N \) nuclei, which can be supposedly located at the space positions, \( \mathbf{R} = \{ \mathbf{R}_i | i = 1, N \} \), and whose atomic numbers are: \( \{ Z_i | i = 1, N \} \).

The discussion about the non-point-like distribution of the nuclear charges is not a new feature, but an old conceptual issue, mainly associated to relativistic frameworks (see for example the exhaustive review by Andrae\(^7\), wherein a large set of possible nuclear charge density forms are described).

In order to simplify the problem while making it adequate for usual MO calculations, here only a Gaussian distribution will be considered. A soft nuclear density \( \rho_S (\mathbf{r} | \mathbf{R}) \) at any point of three dimensional space, \( \mathbf{r} \), can be approximately defined as a linear combination of \( N \) Gaussian functions, centered at the nuclei positions, sharing the same exponent and using the involved atomic numbers as coefficients (Eq. 6),

\[ \rho_S (\mathbf{r} | \mathbf{R}) = \sum_{i=1}^{N} Z_i \prod_{J \neq i} \exp \left( -\frac{(\mathbf{r} - \mathbf{R}_i) \cdot (\mathbf{R}_i - \mathbf{R}_J)}{\alpha} \right) \]

there is an obvious infinity divergence in Eq. (4). Hence, one faces a paradox, that is, a divergence appears for any molecular structure when trying to describe the molecular nuclei charge distributions within an approximate continuous quantum mechanical way, coherent with the electronic cloud description counterpart, while keeping the point-like nature of the nuclear charges.

The only way to recover the classical Coulomb expression (1) from the expression (5) is to rewrite Eq. (4) as as follows:

\[ E_N = \frac{1}{2} \sum_i \sum_{J \neq i} \delta [I \neq J] E_{N,II} \]

Nonetheless, Eq. (4), although being apparently correct, has two drawbacks. First, the diatomic contributions as in Eq. (5) appear twice, and, second, that on taking into account the whole atomic self-repulsion, that is, the diagonal elements of the implicit expression of Eq. (5),

\[ E_{SR} = \sum_i Z_i \prod_{J \neq i} \exp \left( -\frac{(\mathbf{r} - \mathbf{R}_i) \cdot (\mathbf{R}_i - \mathbf{R}_J)}{\alpha} \right) \]

Using the triple product of the monodimensional integrals,
\[
\int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx = \sqrt{\frac{\pi}{\alpha}}
\]

and defining the normalized nuclear atomic shape density as the well-known three dimensional Gaussian (Eq. 7),

\[
\gamma(r|\alpha; R_i) = \left(\frac{\alpha}{\pi}\right)^\frac{3}{2} \exp\left(-\alpha |r - R_i|^2\right)
\] \hspace{1cm} (7)

then one can accordingly write:

\[
\langle \gamma(r|\alpha; R_i) \rangle = \left(\frac{\alpha}{\pi}\right)^\frac{3}{2} \int_0^\infty \exp\left(-\alpha |r|^2\right) \, dr = 1
\]

Taking this soft nuclear density construction, it is now straightforward to demonstrate that the Minkowski norm of the soft nuclear density function is the sum of the nuclear charges or the number of electrons, \(\nu\), of the attached neutral molecular structure. It suffices to rewrite the nuclear density in the equivalent form as follows:

\[
\rho_s(r|\alpha; R) = \sum_i Z_i \gamma(r|\alpha; R_i)
\]

and integrate over all space.

\[
\langle \rho_s(r|\alpha; R) \rangle = \sum_i Z_i \langle \gamma(r|\alpha; R_i) \rangle = \sum_i Z_i = \nu
\]

For a more general form for the nuclear density, the Gaussian exponent can be changed to a different value at each Gaussian function. This will change the Minkowski common normalization factor into a factor similar to that one which appears in Eq. (6), affecting every nuclear Gaussian shape function instead of being a common factor. However, here it has been considered preferable to keep every atomic shape function contribution essentially homogeneous, but allowing for dissimilarity in each atom by means of both the assigned space position of each nucleus and the nuclear charge itself.

The Form of Soft Nuclear Density

It shall be interesting now to briefly sketch the mathematical form of the soft nuclear density for a given molecular structure. For such a purpose, the gradient and Hessian will be described.

Gradient and Hessian

The gradient of the soft nuclear density, as previously described in Eq. (6), corresponds to a \((3\times1)\) column vector, which can be easily described by the compact expression (Eq. 8).

\[
|g| = \nabla \rho_s = \frac{\partial \rho_s(r|\mathbf{R})}{\partial r}
\] \hspace{1cm} (8)

Furthermore, the Hessian of a soft nuclear density corresponds to a \((3\times3)\) matrix, which can be written as Eq. (9),

\[
\mathbf{H} = \nabla \otimes \nabla \rho_s = \frac{\partial^2 \rho_s(r|\mathbf{R})}{\partial r^2}
\]

\[
= 2\alpha \left(\frac{\alpha}{\pi}\right)^\frac{3}{2} \sum_i Z_i \exp\left(-\alpha |r - R_i|^2\right) \mathbf{G}_i
\]

(9)

with the additional definition of a set of \((3\times3)\) matrices defined as:

\[
\forall I : \mathbf{G}_i = \left[2\alpha (r - R_i) \otimes (r - R_i) - \mathbf{I}\right]
\]

Soft nuclear density in atoms

In the case of atoms, the summation appearing in the function itself, and also in the gradient and Hessian, possesses a unique term; the atomic number can be written as \(Z\) and one can choose the position vector as \(\mathbf{R} = 0\). Thus,

\[
\rho_s(r|\alpha; \mathbf{0}) = \left(\frac{\alpha}{\pi}\right)^\frac{3}{2} Z \exp\left(-\alpha |r|^2\right) = Z \gamma(r|\alpha; \mathbf{0})
\]

Using the scale factor, \(\lambda(r) = 2\alpha \left(\frac{\alpha}{\pi}\right)^\frac{3}{2} Z \exp\left(-\alpha |r|^2\right)\), which will depend on the considered space position, for the atomic gradient, \(|g| = -\lambda(r)|r|\), and similarly, the atomic Hessian becomes the symmetric matrix,

\[
\mathbf{H} = \lambda(r) \left[2\alpha (r \otimes r) - \mathbf{I}\right]
\]

Such a result shows that the gradient corresponds to the point position vector, which can be also interpreted as a negative dipole moment operator.
scaled by the nuclear charge distribution and twice the Gaussian exponent, while the Hessian can be easily interpreted as a kind of quadrupole moment tensor, scaled in the same way.

**Soft nuclear dipole moment**

In the same manner, one can deduce kinetic energy; see Ref. 8 for more details. One can devise the formal calculation of the soft nuclear dipole moment as follows:

\[ |\mu| = \langle r \rho_s (r) \rangle = \sum_i Z_i \langle r \gamma (r|x; R_i) \rangle \]

Therefore, the relevant integrals can be described here as follows:

\[ \langle r \gamma (r|x; R_i) \rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \int_B r \exp \left( -\alpha r - R_i \right) d^3 r \]

The integral above can be easily computed for any of the three dipole moment components. Thus,

\[ \left\langle x^2 \gamma (r|x; R_i) \right\rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_B x \exp \left( -\alpha x - X_i \right) dx \]

Then, one can envisage the change of variable, \( u = x - X_i \rightarrow x = u + X_i \rightarrow dx = du \), and therefore it can be also written as

\[ \left\langle x^2 \gamma (r|x; R_i) \right\rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \left( \int_B u \exp \left( -\alpha u^2 \right) du \right) \]

\[ + X_i \int_B \exp \left( -\alpha u^2 \right) du = X_i \]

Consequently it is straightforward to write:

\[ \forall I : \langle r \gamma (r|x; R_i) \rangle = R_i \]

and hence, the soft nuclear dipole moment is coincident with nuclear contribution of the point-like one.

\[ |\mu| = \sum_i Z_i R_i \]

**Soft nuclear quadrupole moment**

The integral of the quadrupole moment can be written as

\[ Q = \langle r \otimes r \rho_s (r) \rangle = \sum_i Z_i \langle r \otimes r \gamma (r|x; R_i) \rangle \]

Thus, a typical integral will be the one corresponding to one of the diagonal elements of the \( r \otimes r \) tensor, i.e.,

\[ Q_{xx} = \langle x^2 \rho_s (r) \rangle = \sum_i Z_i \langle x^2 \gamma (r|x; R_i) \rangle \]

which will correspond to the integral,

\[ \left\langle x^2 \gamma (r|x; R_i) \right\rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_B x^2 \exp \left( -\alpha x - X_i \right) dx \]

Under a similar change of variable as the one used in the dipole moment,

\[ Q_{xx} = \left\langle x^2 \gamma (r|x; R_i) \right\rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_B \left( u + X_i \right)^2 \exp \left( -\alpha u^2 \right) du \]

\[ = \frac{1}{2\alpha} + X_i^2 \]

It is worthwhile to compute the off-diagonal tensor integral.

\[ \left\langle xy \gamma (r|x; R_i) \right\rangle = \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \int_B xy \exp \left( -\alpha x - y \right) d^3 r \]

\[ = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_B x \exp \left( -\alpha x - X_i \right) dx \]

\[ \times \int_B y \exp \left( -\alpha y - Y_i \right) dy \]

However, both the intervening integrals are the ones which can be attached to the dipole moment. Thus, \( Q_{xy} = X_i Y_i \). Therefore, the soft nuclear density attached quadrupole tensor can be written as follows,

\[ Q = \sum_i Z_i \left( \frac{1}{2\alpha} I + R_i \otimes R_i \right) \]
which again, except for a diagonal shift, becomes coincident with the point-like quadrupole tensor.

It is interesting to note now that the point-like moments and their soft nuclear description will be mostly coincident.

**Soft Nuclear Potential**

**Soft Coulomb nuclear repulsion energy**

The possible expression of nuclear repulsion by means of Dirac distributions of nuclear charges permits to consider the transformation of the terms of Eq. (5) into a general formulation, which 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)\(^9,11\). The structure of such an approach has been sketched in the previous section.

Indeed, as Dirac’s delta functions can be considered as the limit of some Minkowski normalized Gaussian function \(\gamma(r | r; R_j)\), as described in Eq. (7), similarly,

\[
\lim_{\alpha \to \infty} \gamma(r | r; R_j) = \delta(r - R_j) \iff \langle \gamma \rangle = \int_0 \gamma(r | r; R_j) dr = 1
\]

and of course in order to be considered Minkowski normalized, the Gaussian function has to be written as described in Eq. (7).

Then, after considering all this straightforward development, the soft nuclear repulsion energy contribution terms can be proposed to be evaluated with the expression, which is the counterpart of the hard nuclear Dirac charge distribution (5),

\[
E_{s,ij} = Z_i Z_j \int_0 \int_0 \left| r_i - r_j \right|^{-1} \gamma(r_i | r; R_j) \gamma(r_j | r; R_i) dr_i dr_j
\]

so that the limit can be directly written as

\[
\lim_{\theta_i, \theta_j \to \infty} E_{s,ij} \to E_{\theta,ij}^N
\]

**Soft nuclear charge distribution**

Then, one may imagine the use of spherical Gaussian functions as a soft nuclear charge density, constituting a family of plausible substitutes of point-like charges, represented by Dirac’s nuclear charge distribution by simply using Eq. (6). This way to describe the nuclear charge distribution can be seen as a linear combination connection between a set of Gaussian space enfoldment points, as recently described\(^1^2\).

Such a nuclear representation is directly related with the so-called promolecular electronic density and the ASA\(^1^3,1^5\) simplified representation of the molecular electronic density function. Generalizing a previous result on atoms by Weinstein et al.\(^1^6\), recently it has been shown that the electronic MEP, generated by such density as described in Eq. (6) is everywhere positive\(^9\). The electronic MEP generated by both a polarized ASA density and a soft potential preserves the classical MEP structure, while eliminating the atomic infinities\(^9,11\).

Thus, the diatomic contributions described as in Eq. (10) will be positive everywhere, but contrary to the usual nuclear repulsion energy properties, will not possess infinity values when nuclei coincide in space.

The corresponding total soft nuclear repulsion energy can be written in accordance of Eq. (4) as

\[
E_s = \int_0 \int_0 \left| r_i - r_j \right|^{-1} \rho_s(r_i) \rho_s(r_j) dr_i dr_j = \sum_{i \neq j} \sum_{j} E_{s,ij}
\]

Explicit integral expression of soft Coulomb nuclear repulsion energy in terms of the incomplete gamma function

It would be interesting to observe and compare the behavior of the soft Coulomb nuclear repulsion (Eq. 10) with respect to the point-like charge limit. In order to obtain an explicit expression for Eq. (10), it is only needed to know the present double integral value. Such an integral has a structure like some simplified electronic repulsion integral over GTO; see for example the work of Saunders\(^1^7\), Shavitt\(^1^8\) or Huizinaga\(^1^9\), and the integrals needed in developing soft EMP\(^9\). Thus, after some simple manipulation it can be written as Eq. (11),

\[
E_s(\theta) = Z_i Z_j \left( \frac{2 \alpha}{\pi} \right)^\frac{3}{2} F_0 \left( \frac{\alpha}{2} \left| R_i - R_j \right|^2 \right)
\]

where \(F_0(x)\) is the incomplete zeroth order gamma function (Ref. 17). The total repulsion energy can be written as

\[
E_s(\theta) = \left( \frac{2 \alpha}{\pi} \right)^\frac{3}{2} \sum_i \sum_j Z_i Z_j F_0 \left( \frac{\alpha}{2} \left| R_i - R_j \right|^2 \right)
\]
The interesting point about the soft Coulomb nuclear repulsion energy is the fact that when the coordinates of two atoms are superimposed, that is, \( R_i = R_j \rightarrow R_{ij} = 0 \), then the point-like charge energy becomes infinite. On the other hand, within the soft nuclear charge scenario one can easily write a finite expression, as in this circumstance \( F_0(0) = 1 \) (Eq. 12).

\[
E_{s,ij}(0) = Z_i Z_j \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{2}} \quad \ldots(12)
\]

One can name the terms of type (12), when referring to a unique kind of atom,

\[
E_{s,ii}(0) = Z_i^2 \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{2}} \quad \ldots(13)
\]

as atomic self-repulsion energy.

For all atoms, then the total self-repulsion energy can be written as,

\[
E_s(\alpha;0) = \sum_i E_{s,ii}(\alpha;0) = \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{2}} \sum_i Z_i^2
\]

that is, total nuclear self-repulsion can be written as some scaled sum of the squares of the nuclear charges. Total soft nuclear self-repulsion is independent of the nuclear positions.

Such nuclear self-repulsion can be employed to structure a nuclear zero energy shift for molecules, which will be independent of the nuclear conformation, but specific for a given set of atoms forming a given molecule.

The self-repulsion nuclear energy thus becomes finite in any circumstances, unless the Gaussian functions exponents become infinite too. Thus, the paradox discussed with respect of the equivalent point-like (Eq. 4), within the soft nuclear charge framework disappears. Due to the infinite self-repulsion energy which the point-like expression has, it can be said that all the possible soft nuclear repulsion energies will appear below the classical one.

**Soft Coulomb nuclear repulsion energy and error function**

Also, the error function and the incomplete gamma function are related by the following expression (see Ref. 20).

\[
F_0(x) = \frac{1}{\sqrt{\pi}} \int_0^x e^{-u^2} du = \frac{1}{\sqrt{\pi}} \text{erf}(\sqrt{x})
\]

Hence, taking into account such equivalence as written above in Eq. (11), for the soft nuclear repulsion terms one can also simply transform the incomplete gamma expression into an error function formulation using

\[
\beta^2 = \frac{\alpha}{2}
\]

Then, Eq. (11) can be easily rewritten as Eq. (14).

\[
E_{s,ij}(R_{ij}) = Z_i Z_j \left( \frac{1}{R_{ij}} \right) \text{erf} \left( \beta R_{ij} \right) = E_{N,ij} \text{erf} \left( \beta R_{ij} \right) \quad \ldots(14)
\]

Consequently, every term of the soft nuclear repulsion energy, expressed as it has been written in Eq. (14), can be seen as the term corresponding to the Coulomb point-like charge repulsion energy in Eq. (5), corrected by a factor made by an error function depending on a constant factor and the internuclear distance.

It is easy to see how Eq. (14) transforms into Eq. (12) when \( R_{ij} = 0 \), because the following limit involving the error function holds

\[
\lim_{x \to 0} \left( \frac{\text{erf}(ax)}{x} \right) = \frac{2a}{\sqrt{\pi}}
\]

Moreover as the error function when the argument is infinity becomes the unit, then another limit holds:

\[
\lim_{x \to \infty} \left( \text{erf}(ax) \right) = 1 \rightarrow \lim_{R_{ij} \to \infty} E_{s,ij}(R_{ij}) = E_{N,ij}
\]

**Soft Electron-Nucleus Interaction**

**Soft nuclear charges and nuclear potential**

Of course, the fact that nuclear charges can be chosen in a softened way within the Coulomb nuclear repulsion expression, does not forbids the use of this characteristic inside the definition of the atomic or molecular local potentials. The classical expression of the nuclear attraction potential operator in a point-like nuclear charge context, which as is well-known, possesses the general form:

\[
V(r) = \sum_i Z_i |r - R_i|^\beta
\]
However, for coherence with the soft nuclear repulsion, the local nuclear attraction potential may be expressed within the soft nuclear charge framework also in a simple way. In this case, the soft one-electron operator, which now includes a spherical Gaussian function for every atomic term, can be readily written as a Coulomb operator (Eq. 15).

\[
V_s (\mathbf{r}) = \sum_i Z_i \int_D \gamma (r_i | \alpha; \mathbf{R}_i) |\mathbf{r} - \mathbf{r}_i|^{-1} \, d\mathbf{r}_i \quad \ldots (15)
\]

On computing the operator matrix expression on a given GTO basis set within the LCAO MO approximation, the operator (15) demands some extra but straightforward analysis.

**Electron-nucleus attraction integrals**

If a pair of general GTO is known, which can be schematically written as

\[
\begin{align*}
&\left\{ \gamma (\mathbf{r}_i | \alpha; \mathbf{R}_i) \right\} \\
&\equiv \gamma_i (\mathbf{r} - \mathbf{R}_i)
\end{align*}
\]

then the matrix element expression within the LCAO MO theory of the soft local nuclear attraction potential as in Eq. (15) can be written, simplifying the GTO notation as follows:

\[
\langle \mu | V_s (\mathbf{r}) | \nu \rangle = \int_D \gamma_\mu (\mathbf{r} - \mathbf{R}_j) \gamma_\nu (\mathbf{r} - \mathbf{R}_k) V_s (\mathbf{r}) \, d\mathbf{r}
\]

\[
= -\sum_i Z_i \int_D \int_D \gamma_\mu (\mathbf{r} - \mathbf{R}_j) \gamma_\nu (\mathbf{r} - \mathbf{R}_k) \gamma (\mathbf{r}_i | \alpha; \mathbf{R}_k) |\mathbf{r}_i - \mathbf{r}_j|^{-1} \, d\mathbf{r}_i \, d\mathbf{r}
\]

where one can easily see that the integrals into the above expression correspond to some kind of simplified three-center repulsion integral structures17,18 taking into account appropriate normalization factors.

**Soft Nuclear Repulsion in Empirical Energy Calculations**

Employing the global atomic coordinate \((N \times 3)\) matrix: \(\mathbf{R} = (\mathbf{R}_1; \mathbf{R}_2; \ldots \mathbf{R}_N)\), the internal energy of a molecular structure within the usual empirical molecular fields, as far as we know and according to the usual procedures in this branch of conformational analysis (see for example a recent discussion in Ref. 21), can be expressed as:

\[
U (\mathbf{R}) = L (\mathbf{R}) + K_0 \sum_{i < j} \frac{Q_i Q_j}{|\mathbf{R}_i - \mathbf{R}_j|} = L (\mathbf{R}) + C_k (\mathbf{R})
\]

The function \(L (\mathbf{R})\) contains terms, using Lennard-Jones type potentials, and expressions taking into account torsional angle, stretching and bending energies. The second term is just a scaled (by the parameter \(K_0\)) Coulomb repulsion computed by means of point-like atomic charges: \(\{Q_i | i = 1, N\}\).

Obviously, when two atoms in the structure studied with the molecular field are coincident, they produce, despite the scaling, the internal system energy infinite, due to the Coulomb term. The chance that this kind of singularities can occur in a medium-large molecular structure has to be roughly proportional to the \(N^2\) objects combinations taken two by two:

\[
C_k^N = \frac{N!}{2!(N-2)!} = \frac{1}{2} N (N - 1)
\]

This troublesome situation can be simply overridden just considering the idea of soft Gaussian charge distributions, which here can be taken for the considered molecular structure as

\[
\rho (\mathbf{r} | \mathbf{R}) = \left( \frac{\alpha}{\pi} \right)^3 \sum_i Q_i e^{-\alpha |\mathbf{r} - \mathbf{R}_i|^2}
\]

where the exponent \(\alpha\) can be considered as a parameter. The Coulombic term may be now expressed by the integral quadratic form:

\[
C_k (\mathbf{R}) = K_s \left( \frac{\alpha}{\pi} \right)^3 \sum_{i < j} Q_i Q_j \times \int_D \int_D |\mathbf{r}_i - \mathbf{r}_j| e^{-\alpha |\mathbf{r}_i - \mathbf{r}_j|^2} \, d\mathbf{r}_i d\mathbf{r}_j
\]

where \(K_s\) can be taken as a scale factor.

Integrals of the type expressed in the equation above, are simply computed in terms of the incomplete gamma function \(F_0 (x)\) or the error function \(erf (x)\).
Thus taking this into account, one can write:

\[
\int_{D}^{D} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} e^{-\alpha \mathbf{r}_1 \cdot \mathbf{r}_2} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\sqrt{\pi}}{2 \pi} \int_{0}^{\infty} \left( \frac{\alpha}{2} \right)^{1/2} |\mathbf{R}_j - \mathbf{R}_j|^2 d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
= \frac{1}{|\mathbf{R}_j - \mathbf{R}_j|^2} \text{erf} \left( \frac{\sqrt{\pi}}{2} |\mathbf{R}_j - \mathbf{R}_j| \right)
\]

The interesting situation now is that when a pair of atoms is coincident, then the outcome is finite.

\[
\int_{D}^{D} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} e^{-\alpha \mathbf{r}_1 \cdot \mathbf{r}_2} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{2 \alpha}{\pi}
\]

A result proving that the soft Coulomb interaction can be written as a corrected point-like sum of binary Coulomb potentials.

\[
C_s (\mathbf{R}) = K_s \sum_{i \neq j} \left( \frac{Q_i Q_j}{|\mathbf{R}_j - \mathbf{R}_j|} \right) \text{erf} \left( \frac{\alpha}{\sqrt{2} |\mathbf{R}_j - \mathbf{R}_j|} \right)
\]

Such soft Coulomb term substitution could have important differences in current conformational empirical analysis and in the protein folding problem.

Also, it could be an interesting point of view in describing the interactions within swarms of atomic or molecular structures.

**Soft self-repulsion terms**

Note that now the double summation does not contain the diagonal terms, which are independent of the molecular conformation and which can be interpreted as a zero internal energy level.

\[
D_s = \sqrt{\frac{2 \alpha}{\pi}} \sum_{i} Q_i^2
\]

Such a term cannot be present in point-like Coulomb expressions.

It is easy to describe the soft Coulomb potential including self-repulsion simply as

\[
C_s (\mathbf{R}) = K_s \left( D_s + \sum_{i \neq j} \left( \frac{Q_i Q_j}{|\mathbf{R}_j - \mathbf{R}_j|} \right) \text{erf} \left( \frac{\alpha}{\sqrt{2} |\mathbf{R}_j - \mathbf{R}_j|} \right) \right)
\]

**Derivatives of the error function**

The practical implementation of the soft Coulomb repulsion term in order to construct adequate geometry optimization procedures asks for the derivatives of the error function (or of the incomplete Gamma function) (see Ref. 20). They are readily computed in terms of Hermite polynomials, according to the simple form:

\[
\forall n = 0,1,2,\ldots: \frac{d^n}{dx^n} \text{erf} (x) = (-1)^n \frac{2}{\sqrt{\pi}} H_n (x) e^{-x^2}
\]

Thus, the first term owing to the fact that \( H_0 (x) = 1 \) corresponds to \( \frac{d}{dx} \text{erf} (x) = \frac{2}{\sqrt{\pi}} e^{-x^2} \).

**Concluding Remarks**

Several aspects of the substitution of the point-like charges by soft nuclear charges in the nuclear contribution to the total molecular energy under the Born-Oppenheimer approximation have been discussed here. The soft nuclear charge distribution has been represented by Minkowski normalized Gaussian functions, centered at each nucleus. After the description of the soft nuclear density function, some applications have been developed without encountering unsurmountable difficulties. The general formalism is well suited to be included in \textit{ab initio} calculations in a Gaussian basis LCAO MO framework. Hence, the molecular total energy surfaces must have preserved the general features, but with the new features in the absence of singularities. In general, total energies will become more positive, as with a soft nuclear density distribution the Coulombic repulsion will be undoubtedly enhanced. This is an interesting viewpoint to take into account within molecular formation and destruction as well as in conformational analysis. The effect of this soft nuclear density feature might slightly modify molecular reactivity.

Use of soft Gaussian nuclear density can have applications in designing fast molecular superposition algorithms to be used in quantum similarity calculations. Subsequent practical applications will be published elsewhere.

**References**