J Math Chem (2013) 51:382–389
DOI 10.1007/s10910-012-0089-4

ORIGINAL PAPER

EMP as a similarity measure: a geometric point of view

Ramon Carbó-Dorca · Emili Besalú

Received: 24 July 2012 / Accepted: 12 September 2012 / Published online: 22 September 2012

Abstract Soft Coulomb potentials constructed by multiplying the classical potential by a Gaussian function (or a linear combination of them) permit to consider a wide family of distributions which limit with the classical potential when the exponent becomes infinite. Soft Coulomb potentials can be employed as potential operators with first order density functions in order to compute families of soft electrostatic molecular potentials (EMP) for any quantum object. The soft EMP family possesses two interesting computational features: being not only formally equivalent to classical EMP, but finite everywhere, even at the atomic nuclei. The structure of the soft Coulomb operator family yielding soft EMP can be easily related with a quantum similarity integral feature.

Keywords Electrostatic molecular potentials (EMP) · Soft coulomb potentials · Soft EMP · Similarity integrals · Density functions origin shift · Soft EMP origin shift

1 Introduction

The study on electrostatic molecular potentials (EMP) since the definition of Scrocco et al. [1] has become a successful current procedure and a widespread tool in quantum chemical literature. A crude search over several assorted publication sources yields more than fifteen thousand references, so just some varied choice of modern work on EMP will be given [2–14] here. However, it must be also stated that the main characteristic trend of published work on EMP corresponds to an uncritical application of the

This paper is dedicated to the memory of Professor Eolo Scrocco, who recently passed away.

R. Carbó-Dorca (✉) · E. Besalú
Institut de Química Computacional, Universitat de Girona, 17071, Girona, Catalonia, Spain
e-mail: quantumqsar@hotmail.com

standard computational procedures, excepting in some limited amount of publications, among these one might quote the work of Gadre [15–21].

In order to justify the aim of this paper, we can say that many years ago in our laboratory we were interested into approximate forms of EMP [22–26] and into the possibility to compare within the quantum similarity framework EMP belonging to different molecular structures [27,28] a path which can be traced in contemporary work by other authors [29,30]. Recently, we were trying to obtain simple but reliable EMP patterns under the atomic shell approximation framework (ASA) (see for more details on ASA for example references [31,32]) continuing an idea which was early introduced [33]. In a novel paper [34], trying to generalize an old result of Weinstein et al. on atomic EMP [35], promolecular ASA density functions (DF) have been demonstrated to be everywhere positive. In the same study has been found that any polarized ASA DF construct appears to be reliable enough to be worth to consider for further research and could be taken as a first step towards the comparative study of two or more EMP.

Taking into account these introductory considerations, the present paper will be constructed in the following way. First, soft charges and Coulomb potentials will be defined and their properties studied. Such preliminary settings will provide the concept of soft EMP next. Then it will be shown that the soft EMP definition permits to consider it as a quantum similarity integral. Finally, a geometric point of view will provide with a final quantum similarity touch the structure of soft EMP.

2 Soft charges and soft Coulomb potentials

In fact EMP corresponds, as it is well-known, to obtain the electrostatic interaction energy between a quantum object, represented by a known first order density function and a positive point charge. Such interaction energy is equivalent to a first order correction to the global electronic energy, when a perturbation is considered with the form of a Coulomb operator with origin at any point $\mathbf{R}$ of three-dimensional Euclidean space, which in atomic units, thus with a unit charge embedded into the operator, can be written as:

$$C(\mathbf{r};\mathbf{R}) = |\mathbf{r}-\mathbf{R}|^{-1}. \tag{1}$$

Recently, we did propose [36] to develop the study of the possibility consisting in the fact that, instead of replacing the supposedly point charge located, at the reference point: $\mathbf{R}$ by a Gaussian distribution as follows.

First, the structure of the EMP interacting point charge can be written even more correctly, using a Dirac distribution, which could be considered implicitly present in Eq. (1):

$$q_\infty = +e\delta(\mathbf{r}-\mathbf{R}). \tag{2}$$

Then, having realized how to write the point charge structure, the point charge (2) might be substituted by a scaled *soft* Gaussian distribution, employing the definition:

$$q_\alpha = \kappa \exp\left(-\alpha \left|\mathbf{r} - \mathbf{R}\right|^2\right) \Rightarrow \lim_{\substack{\alpha \to \infty \\ \kappa = +e}} q_\alpha = q_\infty, \tag{3}$$

where the parameter κ is taken as a real number, which might represent a charge number and can also contain a Minkowski normalization factor for the Gaussian function, which, as it is well-known, in this case can be set to the value: $\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}$. In fact the parameter κ can be considered a scale factor, affecting all the possible manipulations of the soft Coulomb potential.

With this family of soft charges in mind, obviously enough equation (1) transforms into what can be called a *soft* Coulomb potential, which can be written by means of the composite function:

$$C(\mathbf{r}; \mathbf{R} \,|\alpha; \kappa\,) = \kappa \exp\left(-\alpha \left|\mathbf{r} - \mathbf{R}\right|^2\right) \left|\mathbf{r} - \mathbf{R}\right|^{-1}, \tag{4}$$

which in turn transforms into the Coulomb potential (1) as a limit, according to the definition (3). For all the soft Coulomb potentials with finite exponent, the following integral is convergent everywhere in three dimensional space:

$$\forall \mathbf{R} : \langle C\,(\mathbf{r}; \mathbf{R} \,|\alpha; \kappa\,)\rangle = \int_D C\,(\mathbf{r}; \mathbf{R} \,|\boldsymbol{\alpha}; \boldsymbol{\kappa}\,)\, d\mathbf{r} = \kappa \left(\frac{2\pi}{\alpha}\right),$$

a result which can be easily deduced from the chapter of Saunders [37] dedicated to molecular integrals over GTO. Of course, the integral diverges when the exponent reaches the infinite limit value providing the Coulomb potential.

In fact, the previous development just indicates that the whole family of soft Coulomb potentials can be observed as a family of distributions (see for example reference [38] for more details on the distribution concept), with a limit provided by the Dirac's distribution associated to a classical point charge Coulomb potential as described in Eq. (2).

A final remark on the significance of the soft Coulomb potentials can be straightforwardly proposed. The nature of the definition in Eq. (3) is such as not only encompasses the possible description of a first order interaction of a molecular structure with a proton as classical EMP do, but can be used to roughly simulate other heavier cations like Li^+ and similar atomic positive charged atoms.

In fact, to further justify the description of soft Coulomb potentials it can be now noted how accurately the simple ASA atomic DF description [31,32] behave when approximating DF for atoms as linear combinations of Gaussian functions. Also, a related but more involved operator, containing both Gaussian linear combinations and projectors, was constructed many years ago in order to describe within HF theoretical context the atomic cores with the so-called atomic model potential framework, see for

example references [39–42]. Finally, one of us has proposed a comparable solution to take into account nuclear fields in molecular calculations [43].

In this way, if necessary the soft Coulomb potential (3) can be modified in the sense that instead of a unique Gaussian function a linear combination of this kind of functions can be used. The results obtained up to here and the discussion which follows will not be modified.

3 Soft EMP

The electrostatic interaction energy of the soft Coulomb potential (4) and a well-defined first order DF $\rho(\mathbf{r})$ of any quantum object can be now written as:

$$V(\mathbf{R}\,|\alpha;\kappa) = \int_D \rho(\mathbf{r}) C(\mathbf{r};\mathbf{R}\,|\alpha;\kappa)\, d\mathbf{r}. \tag{5}$$

Expression (5) provides a family of quite similar soft EMP, every one of them transforming smoothly into a limiting classical EMP as the soft charge definition in Eq. (3) limits with a classical point charge.

The added interest of such set of functions corresponds to the fact that, for finite values of the parameter α, the soft EMP is finite everywhere. This characteristic permits to look ahead to obtain stable algorithms to be used for similarity comparisons between soft EMP of two or more quantum objects.

4 EMP rethought as a quantum similarity integral

Nevertheless, Eq. (5) not only avoids computational divergence at molecular atomic sites as a main characteristic. Moreover, the soft EMP family can be successfully considered from the point of view of some new kind quantum similarity integral. EMP can be studied in a theoretical similarity way, because when looking at the DF form, one might use a usually forgotten formalism, dividing it into two parts, the positive nuclear ρ_N and the negative electronic ρ_e DF's respectively. One can proceed as follows:

$$\rho(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_e(\mathbf{r}) \tag{6}$$

with the additional general definition:

$$\rho_N(\mathbf{r}) = \sum_I Z_I \delta(\mathbf{r} - \mathbf{R}_I),$$

where $\{Z_I\}$ are atomic numbers and $\{\mathbf{R}_I\}$ the set of molecular atomic coordinates.

Therefore, the EMP expression in Eq. (5) corresponds to a difference of two formally similar integrals:

$$V(\mathbf{R}\,|\alpha;\kappa) = \int_D \rho_N(\mathbf{r})\, C(\mathbf{r};\mathbf{R}\,|\alpha;\kappa)\, d\mathbf{r} - \int_D \rho_e(\mathbf{r})\, C(\mathbf{r};\mathbf{R}\,|\alpha;\kappa)\, d\mathbf{r}. \quad (7)$$

Observing the integral pair in Eq. (7) one can deduce that both correspond to some kind of overlap measure between two distributions. In fact, both of them taken separately can be easily considered quantum similarity measures between a density function and a soft Coulomb distribution.

5 The geometric connection

One of the possible mathematical landscapes from where the soft EMP can be observed also corresponds to a geometrical situation, which as far as the authors know has not been discussed in the literature yet.

The whole state of affairs, which has been debated up to now here, can be also studied starting from the fact that the three function set used in EMP equation (7):

$$P = \{\rho_N(\mathbf{r})\,;\,\rho_e(\mathbf{r})\,;\,C(\mathbf{r};\mathbf{R}\,|\alpha;\kappa)\}$$

can be observed as nothing else than the definition of some triangle within the Hilbert space, where the three functions are described, each function defining one of the triangle vertices.

For positive values of the charge parameter κ, the whole set P belongs to a function semispace, which contains all the non-negative functions which can be defined in the associated Hilbert space. In fact, because the sign of κ, can be either positive or negative and, as commented before, the parameter plays the role of scale factor over the soft Coulomb potential, then it just provides a global change of sign of the resulting soft EMP (7). Thus one can safely consider positive the charge parameter without loss of generality.

Consequently, from this point of view the set P can be safely considered as the vertices of some triangle constructed into some Hilbert semispace. It has been already discussed [44] how the subset of the set $P:\ D = \{\rho_N(\mathbf{r})\,;\,\rho_e(\mathbf{r})\}$ although made of two elements only, becomes linearly dependent upon an origin shift, performed in the way the total DF is defined, as in Eq. (6).

Accordingly, upon such an origin shift operation, the set P, transforms into a new set: $S = \{\rho(\mathbf{r});\, C(\mathbf{r};\mathbf{R}\,|\alpha;\kappa) - \rho_e(\mathbf{r})\} = \{\rho(\mathbf{r});\, F(\mathbf{r};\mathbf{R}\,|\alpha;\kappa)\}$.

In this way, the structure of the original function triangle described by the set P will remain invariant. The origin now will be one of the triangle vertices and consequently, taking into account the set S made of two vectors only, the triangle can be equally well defined.

Hence, it can be thought, that the similarity integral in Eq. (7) corresponding to the soft EMP, can be also evaluated in the geometric framework of the origin shift as provided by the set S and in this way a new similarity integral can be computed:

$$X(\mathbf{r};\mathbf{R}\,|\alpha;\kappa\,)=\int\limits_{D}\rho(\mathbf{r})\,F(\mathbf{r};\mathbf{R}\,|\alpha;\kappa\,)\,d\mathbf{r}=\langle\rho\,(\mathbf{r})F(\mathbf{r};\mathbf{R}\,|\alpha;\kappa\,)\rangle=\langle\rho F\rangle, \quad (8)$$

which using the simplified integral notation provided in the same equation, can be decomposed into four integral terms, which can be easily reduced to two contributions:

$$\langle\rho F\rangle=\langle\rho_N C\rangle-\langle\rho_e C\rangle-\langle\rho_N\rho_e\rangle+\langle\rho_e\rho_e\rangle=V\,(\mathbf{r};\mathbf{R}\,|\alpha;\kappa\,)+Z.$$

The first two integrals correspond to the usual soft EMP as defined in Eq. (7), while the two last ones are constants related with the molecular quantum electronic self-similarity (see, for a modern source with more details on quantum similarity integrals reference [45]):

$$\theta=\langle\rho_e\rho_e\rangle=\int\limits_{D}\rho_e^2\,(\mathbf{r})\,d\mathbf{r}$$

and the overlap quantum similarity integral between the nuclear charge distribution and the electronic density function:

$$\langle\rho_N\rho_e\rangle=\sum_I Z_I\int\limits_{D}\delta\,(\mathbf{r}-\mathbf{R}_I)\rho_e\,(\mathbf{r})\,d\mathbf{r}=\sum_I Z_I\rho_e\,(\mathbf{R}_I),$$

the set $\{\rho_e\,(\mathbf{R}_I)\}$ corresponds to the values of the considered DF at each of the molecular nuclei, the so-called densities at the nuclei.

Then, in general, taking into account these considerations one can write:

$$Z=\theta-\sum_I Z_I\,\rho_e\,(\mathbf{R}_I),$$

corresponding to a constant, which can be related in turn to the origin shift using the electronic energy part of the DF, generating in such a manner an origin shifted soft EMP family.

6 Conclusions and final remarks

The plausible description of a soft EMP permits to substitute the classical Coulomb operator by a family of soft Coulomb potentials, which can act as distributions.

This fact permits to construct for any molecule at any level of the theory a family of soft EMP, which behave practically as the classical EMP but possess the computationally valuable property consisting into that they are everywhere finite, even at the nuclei.

The soft EMP definition also allows reinterpreting the integral, yielding the soft EMP family, as a quantum similarity integral relating three distribution functions.

This set of involved distribution functions permits studying from a geometrical point of view the entire problem of soft EMP evaluation. This fact yields as a result a soft EMP origin shift, connected with electronic quantum selfsimilarity and nuclei-electron interaction.

The computational and practical aspects of the soft EMP procedures under the ASA framework will be published elsewhere [36].

References

1. R.R. Bonnacorsi, E. Scrocco, J. Tomasi, J. Chem. Phys. **52**, 5270–5284 (1970)
2. G. Náray-Szabó, G.G. Ferenczy, Chem. Rev. **95**, 829–847 (1995)
3. P. Politzer, D.G. Truhlar, *Chemical Applications of Atomic and Molecular Electrostatic Potentials* (Plenum, New York, 1981)
4. M. Leboeuf, A.M. Köster, D.R. Salahub, Theor. Chem. Acc. **96**, 23–30 (1997)
5. B. Hernández, F.J. Luque, M. Orozco, J. Comput.-Aided Mol. Design **14**, 329–339 (2000)
6. P. Politzer, J.S. Murray, Theor. Chem. Acc. **108**, 134–142 (2002)
7. S. Van Damme, P. Bultinck, S.J. Fias, Chem. Theory Comput. **5**, 240–334 (2009)
8. Q.-S. Du, C.-H. Wang, Y.-T. Wang, R.-B. Huang, J. Phys. Chem. B **114**, 4351–4357 (2010)
9. T.A. Manz, D.S. Sholl, J. Chem. Theory Comput. **6**, 2455–2468 (2010)
10. L. Leherte, D.P. Vercauteren, J. Comput.-Aided Mol. Des. **25**, 913–930 (2011)
11. S.S. Pingale, Phys. Chem. Chem. Phys. **13**, 15158–15165 (2011)
12. T.A. Manz, D.S. Sholl, J. Chem. Theory Comput. (2012). doi:10.1021/ct3002199 (Just-accepted article)
13. B. Wang, D.G.J. Truhlar, J. Chem. Theory Comput. **8**, 1989–1998 (2012)
14. R.K. Pathak, S.R. Gadre, J. Chem. Phys. **93**, 1770–1773 (1990)
15. S.R. Gadre, I.H. Shrivastava, J. Chem. Phys. **94**, 4384–4390 (1991)
16. S.R. Gadre, S.A. Kulkarni, I.H. Shrivastava, J. Chem. Phys. **96**, 5253–5260 (1992)
17. S.R. Gadre, R.N. Shirsat, A.C. Limaye, J. Phys. Chem. **98**, 9165–9169 (1994)
18. S.R. Gadre, S.A. Kulkarni, C.H. Suresh, I.H. Shrivastava, Chem. Phys. Lett. **239**, 273–281 (1995)
19. K. Babu, V. Ganesh, S.R. Gadre, N.E. Ghermani, Theor. Chem. Acc. **111**, 255–263 (2004)
20. D. Roy, P. Balanarayan, S.R. Gadre, J. Chem. Phys. **129**, 174103 (2008)
21. D. Roy, P. Balanarayan, S.R. Gadre, J. Chem. Sci. **121**, 815–821 (2009)
22. R. Caballol, R. Carbó, M. Martín, Chem. Phys. Lett. **28**, 422–426 (1974)
23. J. Bertrán, E. Silla, R. Carbó, M. Martín, Chem. Phys. Lett. **31**, 267–270 (1975)
24. M. Martín, R. Carbó, C. Petrongolo, J. Tomasi, J. Am. Chem. Soc. **97**, 1338–1347 (1975)
25. R. Carbó, M. Martín, Int. J. Quant. Chem. **9**, 193–214 (1975)
26. R. Carbó, R. Caballol, M. Martín, Anales de Química **76**, 205–213 (1980)
27. R. Carbó, E. Suñé, F. Lapeña, J. Pérez, J. Biol. Phys. **14**, 21–28 (1986)
28. R. Carbó, F. Lapeña, E. Suñé, Afinidad **43**, 483–485 (1986)
29. G. Buchbauer, A. Klinsky, P. Weiß-Greiler, P. Wolschann, J. Mol. Model. **6**, 425–432 (2000)
30. N. Sadlej-Sosnowska, J. Phys. Chem. A **111**, 11134–11140 (2007)
31. L.l. Amat, R. Carbó-Dorca, J. Comput. Chem. **18**, 2023–2029 (1997)
32. L.l. Amat, R. Carbó-Dorca, J. Comput. Chem. **20**, 911–920 (1999)
33. L.l. Amat, R. Carbó-Dorca, J. Chem. Inf. Comput. Sci. **40**, 1188–1198 (2000)
34. R. Carbó-Dorca, E. Besalú, J. Math. Chem. **50**, 981–988 (2012)
35. H. Weinstein, P. Politzer, S. Srebrenik, Theor. Chim. Acta **38**, 159–163 (1975)
36. E. Besalú, R. Carbó-Dorca, *Softened Electrostatic Molecular Potentials*, IQC Technical Report TR-2012-3 (2012)
37. V.R. Saunders, *An introduction to Molecular Integral Evaluation*, in Diercksen et al. (eds.) *Computational techniques in Quantum Chemistry and Molecular Physics* (D. Eidel Pub. Co., Dordrecht, 1975) pp. 347–424
38. G.A. Korn, Th. M. Korn, *Mathematical Handbook for Scientists and Engineers* (Dover Publications, New York, 2000)
39. V. Bonifacic, S. Huzinaga, J. Chem. Phys. **60**, 2779–2787 (1974)
40. D. McWilliams, S. Huzinaga, J. Chem. Phys. **63**, 4678–4685 (1975)

41. O. Gropen, S. Huzinaga, A.D. McLean, J. Chem. Phys. **73**, 402–407 (1980)
42. Y. Sakai, S. Huzinaga, J. Chem. Phys. **76**, 2537–2552 (1982)
43. R. Carbó-Dorca, J. Math. Chem. **38**, 671–676 (2005)
44. R. Carbó-Dorca, E. Besalú, J. Math. Chem. **50**, 1161–1178 (2012)
45. R. Carbó-Dorca, E. Besalú, L.D. Mercado, J. Comp. Chem. **32**, 582–599 (2011)