

# On the nature of atomic shell approximation (ASA) electrostatic molecular potentials (EMP)

Ramon Carbó-Dorca · Emili Besalú

Received: 13 September 2011 / Accepted: 9 November 2011 / Published online: 19 November 2011  
© Springer Science+Business Media, LLC 2011

**Abstract** General properties of the electrostatic molecular potential (EMP) when obtained by means of the atomic shell approximation (ASA) density function (DF) are discussed. In the present study it is proved that in general and without exceptions promolecular ASA DF provide EMP which are everywhere repulsive. The polarized ASA DF version, providing an alternative enhanced kind of EMP, behaves in such a way that in the neighborhood of negative charged atoms, attractive regions appear resembling the *ab initio* results.

**Keywords** Molecular electrostatic potentials (MEP) · Atomic shell approximation (ASA) · Density functions (DF) · Promolecular ASA DF · Polarized ASA DF

## 1 Introduction

Electrostatic molecular potentials (EMP) have been, since the first definition by Scrocco et al. [1], a widespread tool of quantum chemistry. Long time ago Giessner-Prettre and Pullman [2] reported faulty behavior when EMP were computed with approximate density functions (DF), constructed with spherical s-type basis set functions. We have tested the EMP behavior within the atomic shell approximation (ASA) DF [3–7] with several levels of construction over varied molecular structures and noticed that within the so-called promolecular level ASA DF, EMP become everywhere repulsive.

Thus, the aim of the present paper will consist to prove without doubt that, under the approach of promolecular ASA DF constructed with s-type GTO, the associated ASA EMP always will be everywhere positive. However, the EMP maps obtained, while giving the same picture than the DF ones, might provide enhanced hydrogen

---

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

contributions. Also it will be discussed that the ASA EMP version, constructed with a polarized ASA DF, where the promolecular atomic numbers are substituted by gross atomic populations, might behave in the same way as the promolecular ASA EMP, but in the neighborhood of negatively charged atoms, attractive EMP zones resembling the ab initio EMP ones might appear.

## 2 Description of the ASA EMP

Any ASA molecular DF can be written using the approximate expression:

$$\rho_M(\mathbf{r}) = \sum_{I \in M} Q_I \rho_I(\mathbf{r} - \mathbf{r}_I) \quad (1)$$

where  $\{Q_I\}$  can be atomic numbers in promolecular versions or gross atomic populations in polarized versions. One can also take into account that the ASA [6] atomic DF moiety in Eq. (1) can be written as:

$$\rho_I(\mathbf{r} - \mathbf{r}_I) = \sum_{\lambda \in I} \omega_\lambda^I \sigma_\lambda^I(\mathbf{r} - \mathbf{r}_I) \quad (2)$$

being:  $\{\sigma_\lambda^I(\mathbf{r} - \mathbf{r}_I)\}$  a set of Minkowski normalized 1s GTO, the ASA basis set, and  $\{\omega_\lambda^I\}$  a set of convex coefficients:  $\sum_{\lambda \in I} \omega_\lambda^I = 1$ . Both ASA basis set and convex coefficients are optimally fitted [5, 7] to ab initio atomic orbitals of the atom in question.

Accordingly, the approximate ASA EMP associated to DF of type (1) can be obtained with an expression like:

$$V_M(\mathbf{h}) = \sum_{I \in M} \frac{Z_I}{|\mathbf{h} - \mathbf{r}_I|} - \sum_{I \in M} Q_I \int_D \frac{\rho_I(\mathbf{r} - \mathbf{r}_I)}{|\mathbf{h} - \mathbf{r}|} d\mathbf{r}.$$

One can immediately see that such an approximate EMP can be written by using an EMP atomic contribution which can be defined as:

$$V_I(|\mathbf{h} - \mathbf{r}_I|) = \frac{Z_I}{|\mathbf{h} - \mathbf{r}_I|} - Q_I \int_D \frac{\rho_I(\mathbf{r} - \mathbf{r}_I)}{|\mathbf{h} - \mathbf{r}|} d\mathbf{r} = \frac{Z_I}{|\mathbf{h} - \mathbf{r}_I|} - Q_I U_I(|\mathbf{h} - \mathbf{r}_I|) \quad (3)$$

In the equation above, the dependence on the vector difference modulus:  $|\mathbf{h} - \mathbf{r}_I|$  appearing as a variable within the atomic ASA EMP contribution is due to the spherical symmetry of ASA DF basis set. Then, in using such a partition the ASA EMP could be finally expressed as the sum over the atoms in the studied molecule:

$$V_M(\mathbf{h}) = \sum_{I \in M} V_I(|\mathbf{h} - \mathbf{r}_I|).$$

The EMP electronic atomic integral terms of Eq. (3) can be written using the ASA DF terms as defined in Eq. (2), like:

$$U_I(|\mathbf{h} - \mathbf{r}_I|) = \sum_{\lambda \in I} \omega_{\lambda}^I \int_D \frac{\sigma_{\lambda}^I(\mathbf{r} - \mathbf{r}_I)}{|\mathbf{h} - \mathbf{r}|} d\mathbf{r} = \sum_{\lambda \in I} \omega_{\lambda}^I u_{\lambda}^I(|\mathbf{h} - \mathbf{r}_I|) \quad (4)$$

### 3 Involved integral expressions for atomic EMP ASA basis set terms

The integrals over the ASA basis set for every atom appearing in Eq. (4) can be expressed as [4, 7]:

$$u_{\lambda}^I(|\mathbf{h} - \mathbf{r}_I|) = 2 \left( \frac{\alpha_{\lambda}^I}{\pi} \right)^{\frac{1}{2}} F_0 \left( \alpha_{\lambda}^I |\mathbf{h} - \mathbf{r}_I|^2 \right)$$

and also the zeroth order incomplete gamma function can be rewritten [8] as well as:

$$F_0 \left( \alpha_{\lambda}^I |\mathbf{h} - \mathbf{r}_I|^2 \right) = \int_0^1 \exp \left( -\alpha_{\lambda}^I |\mathbf{h} - \mathbf{r}_I|^2 t^2 \right) dt,$$

which is a well-known expression permitting to write alternatively the incomplete gamma function by means of the error function:

$$F_0(x) = \frac{1}{2} \left( \frac{\pi}{x} \right)^{\frac{1}{2}} \operatorname{erf} \left( x^{\frac{1}{2}} \right).$$

Therefore, one can also express the atomic terms contribution to the EMP for every ASA basis set function as:

$$u_{\lambda}^I(|\mathbf{h} - \mathbf{r}_I|) = \frac{1}{|\mathbf{h} - \mathbf{r}_I|} \operatorname{erf} \left( \left( \alpha_{\lambda}^I \right)^{\frac{1}{2}} |\mathbf{h} - \mathbf{r}_I| \right)$$

### 4 Inequalities

However, as the error function has a range within the interval [0,1] for positive arguments, then one can easily deduce that for any ASA basis function one will have necessarily:

$$u_{\lambda}^I(|\mathbf{h} - \mathbf{r}_I|) \leq \frac{1}{|\mathbf{h} - \mathbf{r}_I|}$$

and then, one can also write the complete convex atomic ASA linear combination as fulfilling:

$$\sum_{\lambda \in I} \omega_{\lambda}^I u_{\lambda}^I (|\mathbf{h} - \mathbf{r}_I|) \leq \frac{1}{|\mathbf{h} - \mathbf{r}_I|}.$$

Thus, there are chances that the following inequalities are accomplished:

$$\frac{Z_I}{|\mathbf{h} - \mathbf{r}_I|} \geq Q_I U_I (|\mathbf{h} - \mathbf{r}_I|) \rightarrow V_I (|\mathbf{h} - \mathbf{r}_I|) \geq 0 \rightarrow V(\mathbf{h}) \geq 0,$$

because one can also write the ASA total atomic electronic contribution to EMP as:

$$U_I (|\mathbf{h} - \mathbf{r}_I|) = \frac{1}{|\mathbf{h} - \mathbf{r}_I|} \sum_{\lambda \in I} \omega_{\lambda}^I \operatorname{erf} \left( \left( \alpha_{\lambda}^I \right)^{\frac{1}{2}} |\mathbf{h} - \mathbf{r}_I| \right) = \frac{\Omega_I}{|\mathbf{h} - \mathbf{r}_I|}$$

with the ancillary definition and a connected inequality:

$$\Omega_I = \sum_{\lambda \in I} \omega_{\lambda}^I \operatorname{erf} \left( \left( \alpha_{\lambda}^I \right)^{\frac{1}{2}} |\mathbf{h} - \mathbf{r}_I| \right) \leq 1;$$

thus, in this way every ASA EMP atomic term can be compactly written like:

$$\forall I : V_I (|\mathbf{h} - \mathbf{r}_I|) = \frac{Z_I}{|\mathbf{h} - \mathbf{r}_I|} - Q_I U_I (\mathbf{h} - \mathbf{r}_I) = \frac{Z_I - \Omega_I Q_I}{|\mathbf{h} - \mathbf{r}_I|}.$$

## 5 Discussion

From the previous ASA EMP formulation, a discussion can be easily carried out; revealing that the ASA EMP will always become a positive function. Two relevant cases can be discussed:

### a) Promolecular case

In promolecular ASA DF expansions the gross atomic populations are coincident with atomic numbers. Hence, if  $\forall I : Q_I = Z_I$ ; then, clearly in this case:  $\forall I : V_I (|\mathbf{h} - \mathbf{r}_I|) > 0 \rightarrow V_M(\mathbf{h}) > 0$ , and there are no chances of appearance of negative regions in promolecular ASA EMP cases. Promolecular ASA EMP's are everywhere repulsive for any neutral molecular structure.

### b) Polarized ASA DF case

When using the polarized ASA DF description though, the gross atomic population is in general not coincident with the corresponding atomic number. As polarizations are due to positive or negative deviations from the atomic number charge, two situations can arise:

#### b.1) Some nucleus are positively charged:

If  $\exists I : Q_I < Z_I$ , then:  $V_I (|\mathbf{h} - \mathbf{r}_I|) > 0$

b.2) Some nucleus negatively charged:

If  $\exists I : Q_I > Z_I \wedge Q_I = \alpha Z_I$ ; then, as  $\alpha > 1$ , if:  $\alpha \Omega_I > 1 \rightarrow V_I(|\mathbf{h} - \mathbf{r}_I|) < 0$

and this situation opens the possible appearance of regions with global ASA EMP negative values, whenever the sum of ASA potential atomic elements is dominated by the negative ASA atomic terms.

However, one must take into account that the scaling parameter  $\alpha$  can be associated to the variation within a quite reduced interval:  $\alpha \in [1.0; 1.15]$ . One can take generously the upper bound value of  $\alpha$  for second row atoms; otherwise the resulting polarized atomic populations perhaps become unphysical for neutral molecules. Also this upper bound will depend of the reciprocal of atomic number, thus becoming lesser as atomic numbers grow. This is so because, when observing gross atomic populations for second row atoms, one can hardly find such a large deviation from the atomic number.

Supposing this physically acceptable upper bound interval for  $\alpha$ , then the value of  $\Omega_I$  to yield a product:  $\alpha \Omega_I > 1$ , has to be approximately around  $\Omega_I \geq 0.87$ ; this last condition might be usually met in practical calculations, in the neighbourhoods of most polarized atoms like nitrogen, oxygen and fluorine.

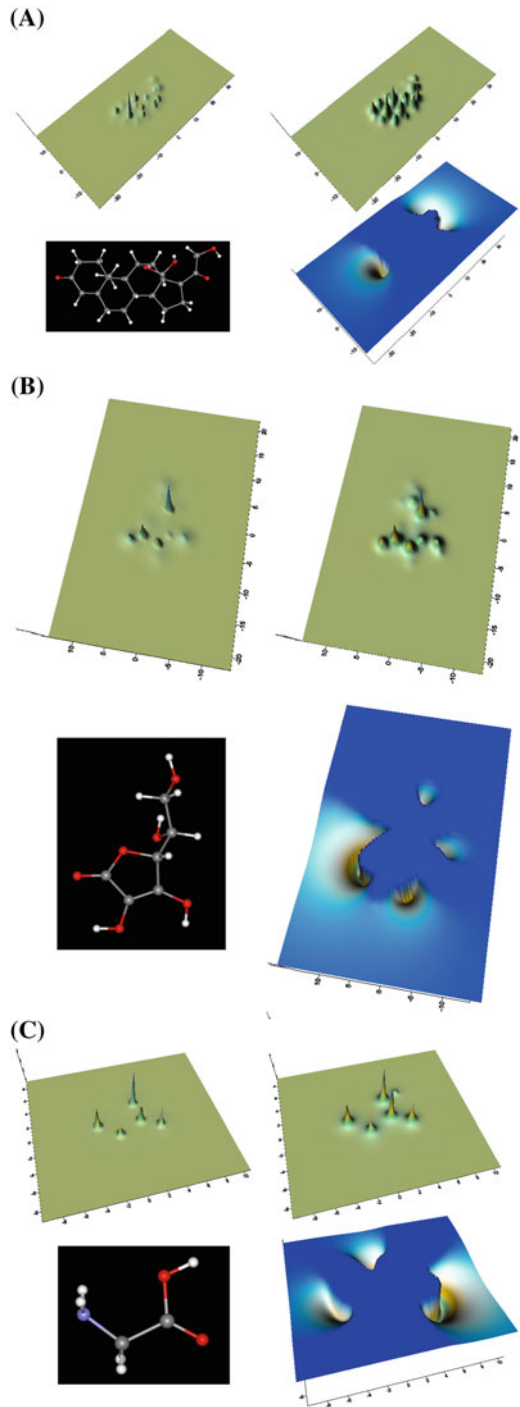
Other kinds of numerical analysis are imaginable, but in all the cases the mathematical possibility in neutral molecules to bear extremely negative charged atoms ( $Q_I \gg Z \leftrightarrow \alpha \gg 1$ ) appears not so common or unphysical. As a consequence, it could happen that EMP acquires high positive values when using polarized ASA DF framework but also some negative regions might appear. The appearance of negative regions in the neighbourhood of negative charged atoms is a fact which can be seen in some tests presented below and of course in other similar cases. However, the absolute values of the polarized ASA EMP negative regions, at least for the studied structures, is one order of magnitude less than the usual mean values of the positive ones, but quite relevant when properly scaled and possessing a graphical appearance similar to the ab initio EMP models.

Resuming: in all the studied cases, the ASA EMP possesses an appearance quite isomorphic to the associated ASA DF, with the added feature, consisting in that, due to the higher values in the neighbourhood of the atomic potential discontinuities, the hydrogen atoms appear enhanced with respect to the DF maps. Moreover, computational tests have shown a polarized ASA EMP behaviour similar to the promolecular case, but with the appearance of negative EMP values around negatively charged atoms. This feature can be easily drawn with a rescaling and further employed as a way to obtain with the polarized ASA DF framework EMP maps resembling the ab initio ones.

## 6 Graphical examples of polarized ASA EMP

As a visual example of this situation for polarized ASA EMP and in order to compare the graphical behaviour between polarized ASA DF and EMP, Fig. 1a, b, c show for several assorted molecules (aldosterone, ascorbic acid and glycine respectively) a polarized ASA DF map, the polarized ASA EMP map counterpart, the associated

**Fig. 1** Functional maps for three chosen molecular structures. Starting from *upper left* and clockwise: polarized ASA DF at XY plane, polarized ASA EMP at XY plane, in *blue* the zoomed rescaling of the negative region at the XY plane of the polarized ASA EMP, molecular ball and stick representation with XY plane in *black*. **a** Aldosterone. **b** Ascorbic acid. **c** Glycine (Color figure online)



molecular structure and the zoomed map of polarized ASA EMP negative region as well.

Calculations of geometry and atomic populations have been performed under Spartan program [9] and the graphical part has been obtained via Surfer code [10]. The polarized ASA DF and EMP grids have been computed via a specific program integrated within the Molecular Quantum Similarity Program Suite [11]. Such a program and some input and output examples can be downloaded from a public web site [12].

It must be noted that in the three provided examples the rescaled attractive polarized ASA EMP region in the chosen XY plane, presents the typical EMP negative wells in the vicinity of the negatively charged oxygen and nitrogen atoms. Indicating that for polarized molecules this version of ASA EMP might behave with a similar topology as in a more accurate computational environment.

## 7 Conclusions

Promolecular ASA description of the DF defines in general EMP for any molecular structure, which will present positive regions only. Therefore whatever molecule considered, promolecular EMP will be everywhere repulsive.

When gross atomic populations are used in the promolecular definition instead of atomic numbers, providing the polarized ASA DF version, then there is the possibility that some atomic contributions to the ASA EMP might become negative, essentially when the associated gross atomic population is greater than the atomic number charge. In three dimensional space regions where such negative terms become dominant, there is a possibility that the EMP becomes attractive. However, in atoms where the gross atomic population is less than the atomic number the corresponding atomic EMP contribution will be always positive. Due to the slight deviation from atomic numbers of the gross atomic populations it might be possible that, even within the framework of polarized ASA DF, the derived ASA EMP becomes negative but with absolute values one order of magnitude less than the positive regions mean value.

Thus, contrarily to ASA DF, which produces sufficiently accurate molecular electronic density, ASA EMP doesn't possess such an adequate trend. In fact, ASA EMP matches and enhances topologically the former ASA DF. Finally polarized ASA EMP can provide negative regions around the neighbourhood of atoms with atomic populations with values higher than the atomic numbers.

**Acknowledgments** The authors want to acknowledge the useful comments of the referees, which have helped to improve the presentation of the original manuscript and even vary slightly the conclusions in the polarized ASA EMP case.

## References

1. R. Bonnacorsi, E. Scrocco, J. Tomasi, *J. Chem. Phys.* **52**, 5270 (1970)
2. C. Giessner-Prettre, A. Pullman, *Theor. Chim. Acta* **37**, 335 (1975)
3. P. Constans, R. Carbó, *J. Chem. Inf. Comput. Sci.* **35**, 1046 (1995)

4. P. Constans, X. Fradera, Ll. Amat, R. Carbó, Quantum molecular similarity measures (QMSM) and the atomic shell approximation (ASA), in Proceedings of the 2nd Girona Seminar on Molecular Similarity. July 1995. Advances in Molecular Similarity. (JAI Press Inc., Greenwich, 1996), 1, p. 187
5. Ll. Amat, R. Carbó-Dorca, *J. Comput. Chem.* **18**, 2023 (1997)
6. Ll. Amat, R. Carbó-Dorca, *J. Comput. Chem.* **20**, 911 (1999)
7. Ll. Amat, R. Carbó-Dorca, *J. Chem. Inf. Comput. Sci.* **40**, 1188 (2000)
8. V.R. Saunders, in An Introduction to Molecular Integral Evaluation, ed. by G.H.F. Diercksen, B. T. Sutcliffe, A. Veillard. (D. Reidel Publishing Co., Dordrecht, 1975), p. 347
9. Spartan '10. version 1.1.0 (Wavefunction Inc., Irvine, 2011)
10. Surfer V8.02, (Golden Software Inc., Golden, 2002)
11. R. Carbó-Dorca, E. Besalú, L.D. Mercado, *J. Comp. Chem.* **32**, 582–599 (2011)
12. <http://iqc.udg.edu/~quantum/software/MQSPS/ASAEPM/>