

On robust density fitting in molecules and extended systems

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Abstract Two theorems for robust density fitting are proved: A. For a given electron density, the best robust density fitting approximation to the Coulomb electron repulsion energy results from the unconstrained Coulomb metric fit, B. For infinite periodic systems, the necessary condition for correct long-range behavior of any robust density fitting approximation of the Coulomb electron repulsion energy is the exact reproduction of the number of electrons.

Keywords Electron density fitting · Robust fitting · Coulomb metric · Extended systems

1 Introduction

Electron density is a key quantity for our understanding of both molecular and bulk properties of matter. Fundamental theorems concerning the electron density were established in the past, e.g. the Hohenberg-Kohn theorem [1] or the Holographic electron density theorem [2], to mention those of crucial importance. However, the quantities depending on electron density are not always easy to evaluate; quantities containing two-electron integrals are usually a bottleneck of a practical calculation. Techniques how to handle this problem effectively are evidently of considerable interest.

Density fitting (DF)—also referred to as the resolution of the identity method—has become a powerful tool to speed up electronic structure calculations for both molecular [3–8] and extended systems [9–11], mainly in connection with approximation of time-consuming two-electron Coulomb repulsion integrals. The basic idea is to approximate

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the electron density ρ , by expansion in an auxiliary basis set. The expansion coefficients are determined using a suitable optimization criterion which is usually the minimization of the error integral $(\rho - \tilde{\rho}|\Omega_{12}|\rho - \tilde{\rho})$ with Ω_{12} being a metric operator. [Throughout the text the notation $(\rho_1|\Omega_{12}|\rho_2) = \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_1^*(\mathbf{r}_1) \Omega(\mathbf{r}_1, \mathbf{r}_2) \rho_2(\mathbf{r}_2)$ will be used with a special case $(\rho_1|\rho_2)$ for $\Omega_{12} = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ and $\langle \rho_1|\rho_2 \rangle$ for $\Omega_{12} = \delta(\mathbf{r}_1 - \mathbf{r}_2)$. Tilde is used to denote fitted quantities.]

Independently, the theory was formulated using either the overlap ($\Omega_{12} = \delta(\mathbf{r}_1 - \mathbf{r}_2)$) [12] or Coulomb ($\Omega_{12} = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$) [13] metric. A tunable bridging of both was suggested for large scale systems [14], in some cases a charge-preserving constrained fit [12, 15] can be advantageous. A natural question arises which of the possibilities is the best. Of course, if auxiliary basis sets were complete the question would be irrelevant. In practice, the answer depends on the reason for which the fit is used. Intuitively, one feels that if the reason is to approximate Coulomb repulsion integrals, the use of Coulomb metric should be the best. Without proof, this was already stated by Dunlap et al. [16]. From results on a set of molecular systems Vahtras et al. [3] concluded that the Coulomb metric is superior to overlap criterion or to a combination of both with an explanation that the Coulomb fitting metric mimics the Coulomb field rather than the charge distribution. This served as a justification for working with Coulomb metric DF [17–19] until a robust fit concept was introduced [20, 21] and it was recognized that the poor performance of non-Coulomb metric fits is caused rather by the fact that these fits are not robust. Obviously, each non-robust fit can be easily made robust, generally for the price of doubling the computational expenses. This makes non-Coulomb metric DF competitive with the Coulomb one [22, 23]. Non-Coulomb metric fits turned out to be of considerable importance for large scale [14] and extended systems [11, 24] where the slow decay of Coulomb matrices caused problems.

Working with robust DF, the question which of the robust fits is the best should be answered. With regard to Coulomb repulsion the unconstrained Coulomb metric fit happens to be directly both robust and variational. Considering this one naturally expects the Coulomb metric fit to be the best of robust fits as well. Below a proof is given that this is indeed the case (Theorem 1).

Infinite systems with translational periodicity exhibit features which are not present in the molecular case [25]. It is a well-known fact that for these systems the Coulomb electron repulsion energy contribution E , contains (due to the slow Coulomb decay of long-range contributions) a term with a divergent infinite sum. For a charge neutral systems this term fortunately exactly cancels against its attractive counterpart [26, 27]. Of course, once we want to approximate E it is of crucial importance for any approximation to have exactly the same divergent part no matter how the approximation was made, otherwise the divergent terms would never exactly cancel and, the total energy (per unit cell) would never converge to a finite value no matter how large cluster we would consider. The necessary condition for this to be guaranteed was already analyzed in [24]. As a by-product of the way of derivation of Theorem 1, in this letter we offer an alternative way of proving this for a robust fit (Theorem 2).

Theorem 1 *For a given electron density, the best robust DF approximation to the Coulomb electron repulsion energy results from the unconstrained Coulomb metric fit.*

Proof The Coulomb electron repulsion energy contribution E can be expressed as

$$E = \frac{1}{2}(\rho|\rho) \quad (1)$$

with ρ being the electron density. Within the DF approach, ρ is approximated by expansion into an auxiliary basis set, $\{\theta\}$,

$$\rho(\mathbf{r}) \approx \tilde{\rho}(\mathbf{r}) = \sum_u \theta_u(\mathbf{r})C_u. \quad (2)$$

Regardless of the way how the expansion coefficients in (2) are determined the robust DF approximation to (1) reads [21]

$$E \approx \tilde{E} = \frac{1}{2}(\rho|\tilde{\rho}) + \frac{1}{2}(\tilde{\rho}|\rho) - \frac{1}{2}(\tilde{\rho}|\tilde{\rho}). \quad (3)$$

Substituting for $\tilde{\rho}$ from (2) we have (for lucidity of formulas let us work with $2E$ in the following),

$$2\tilde{E} = \mathbf{J}^\dagger \mathbf{C} + \mathbf{C}^\dagger \mathbf{J} - \mathbf{C}^\dagger \mathbf{V}^{-1} \mathbf{C} \quad (4)$$

with \mathbf{J} being a column vector and \mathbf{V} a square matrix with matrix elements $J_u = (\theta_u|\rho)$ and $V_{u,u'} = (\theta_u|\theta_{u'})$, respectively. Equation (4) can be rewritten to

$$2\tilde{E} = \mathbf{J}^\dagger \mathbf{V}^{-1} \mathbf{J} - (\mathbf{J} - \mathbf{V}\mathbf{C})^\dagger \mathbf{V}^{-1} (\mathbf{J} - \mathbf{V}\mathbf{C}). \quad (5)$$

Since \mathbf{V} is a positive definite matrix, so will be \mathbf{V}^{-1} and, consequently,

$$\mathbf{J}^\dagger \mathbf{V}^{-1} \mathbf{J} \geq 0 \quad (6)$$

$$(\mathbf{J} - \mathbf{V}\mathbf{C})^\dagger \mathbf{V}^{-1} (\mathbf{J} - \mathbf{V}\mathbf{C}) \geq 0 \quad (7)$$

Realizing that $E = \tilde{E} + (\rho - \tilde{\rho}|\rho - \tilde{\rho})/2$ for a robust fit and making use of positivity of the pertinent Coulomb integral it is also evident that [16]

$$E \geq \tilde{E} \quad (8)$$

Considering now (6)–(8), from (5) we immediately see that \tilde{E} will be maximal (and, closest to E) when \mathbf{C} is such that $\mathbf{J} - \mathbf{V}\mathbf{C} = \mathbf{0}$, i.e.,

$$\mathbf{C} = \mathbf{V}^{-1} \mathbf{J} \quad (9)$$

which is just the case of Coulomb metric without any additional constraints (see e.g. [3]). Evidently, with any other choice of \mathbf{C} 's than (9), \tilde{E} will always be worse.

Notice that the theorem can be easily generalized to hold for any two-electron integral of the type $(\rho_{ab}|\rho_{ab})$ with $\rho_{ab}(\mathbf{r}) = \chi_a^*(\mathbf{r})\chi_b(\mathbf{r})$. In complete analogy, one can

also prove that using the unconstrained overlap metric results in the best fit for four-center overlaps $\langle \rho_{ab} | \rho_{ab} \rangle$ which occur e.g. in grid-free density functional calculations [28, 22].

In practice, for some reason (e.g., for large or extended systems) it may turn out to be advantageous to use different fitting criterion than the optimal one. In such a case Eq. (5) offers a simple possibility to assess how far from the best possible fit we are. Our experience is that—if non-zero—the second term in (5) is numerically only a small correction to the leading term $\mathbf{J}^\dagger \mathbf{V}^{-1} \mathbf{J}$.

The nice form of the formula (5) will be utilized also in the proof of the following theorem. \square

Theorem 2 *For infinite periodic systems, the necessary condition for correct long-range behavior of any robust DF approximation of the Coulomb electron repulsion energy is the exact reproduction of the number of electrons.*

Proof For infinite periodic systems the Coulomb electron repulsion energy per unit cell can be rewritten as

$$E = (\text{regular terms}) + \frac{1}{2} n_e^2 \sum_{R>} \frac{1}{R} \quad (10)$$

where the regular part contains all the short range terms plus the long range multipole expansion contributions beyond the 0-th order (charge-charge) term ($R>$ indicates long-range summation, n_e stands for the number of electrons per unit cell)

Let us separate the singular part out of Coulomb integrals V and J in a similar way (see [29])

$$\mathbf{V} = \mathbf{V}_0 + L \mathbf{s} \mathbf{s}^\dagger \quad (11)$$

$$\mathbf{J} = \mathbf{J}_0 + L \mathbf{s} n_e \quad (12)$$

where \mathbf{s}^\dagger is a row vector with matrix elements $s_u = \langle 1 | \theta_u \rangle$, and L is the (divergent) long-range Coulomb sum in (10), $L = \sum_{R>} \frac{1}{R}$.

Substituting now (11) and (12) into (5) after a little algebra we get

$$2\tilde{E} = \mathbf{J}_0^\dagger \mathbf{V}_0^{-1} \mathbf{J}_0 - (\mathbf{J}_0 - \mathbf{V}_0 \mathbf{C})^\dagger \mathbf{V}_0^{-1} (\mathbf{J}_0 - \mathbf{V}_0 \mathbf{C}) - L(\tilde{n} - n_e)^2 + L n_e^2 \quad (13)$$

where $\tilde{n} = \mathbf{s}^\dagger \mathbf{C}$. Integrating (2) it can be immediately shown that \tilde{n} is the DF-approximation to the number of electrons regardless of the choice of \mathbf{C} 's. Since the first two terms in (13) are regular, from comparison of (13) with (10) now Theorem 2 follows.

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References

1. P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B864 (1964)
2. P.G. Mezey, *Mol. Phys.* **96**, 169 (1999)
3. O. Vahtras, J. Almlöf, M.W. Feyereisen, *Chem. Phys. Lett.* **213**, 514 (1993)
4. F.R. Manby, P.J. Knowles, A.W. Lloyd, *J. Chem. Phys.* **115**, 9144 (2001)
5. H.-J. Werner, F.R. Manby, P.J. Knowles, *J. Chem. Phys.* **118**, 8149 (2003)
6. S. Ten-no, F.R. Manby, *J. Chem. Phys.* **119**, 5358 (2003)
7. R. Polly, H.-J. Werner, F.R. Manby, P.J. Knowles, *Mol. Phys.* **102**, 2311 (2004)
8. F. Weigend, *J. Comput. Chem.* **29**, 167 (2008)
9. G. te Velde, E.J. Baerends, *Phys. Rev. B* **44**, 7888 (1991)
10. Š. Varga, M. Milko, J. Noga, *J. Chem. Phys.* **124**, 034106 (2006)
11. L. Maschio, D. Usvyat, F.R. Manby, S. Casassa, C. Pisani, M. Schütz, *Phys. Rev. B* **76**, 075101 (2007)
12. E.J. Baerends, D.E. Ellis, P. Ros, *Chem. Phys.* **2**, 41 (1973)
13. J.L. Whitten, *J. Chem. Phys.* **58**, 4496 (1973)
14. Y. Jung, A. Sodt, P.M.W. Gill, M. Head-Gordon, *Proc. Natl. Acad. Sci. USA* **102**, 6692 (2005)
15. B.I. Dunlap, *J. Mol. Struct. (Theochem)* **501–502**, 221 (2000)
16. B.I. Dunlap, J.W.D. Connolly, J.R. Sabin, *J. Chem. Phys.* **71**, 3396 (1979)
17. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **240**, 283 (1995)
18. F. Weigend, M. Häser, *Theor. Chem. Acc.* **97**, 331 (1997)
19. C. Hättig, F. Weigend, *J. Chem. Phys.* **113**, 5154 (2000)
20. B.I. Dunlap, *Phys. Chem. Chem. Phys.* **2**, 2113 (2000)
21. B.I. Dunlap, *J. Mol. Struct. (Theochem)* **529**, 37 (2000)
22. Š. Varga, *J. Chem. Phys.* **127**, 114108 (2007)
23. S. Reine, E. Tellgren, A. Krapp, T. Kjærgaard, T. Helgaker, B. Jansik, S. Høst, P. Salek, *J. Chem. Phys.* **129**, 104101 (2008)
24. Š. Varga, *Int. J. Quantum Chem.* **108**, 1518 (2008)
25. J.-L. Calais, *Int. J. Quantum Chem.* **58**, 307 (1996)
26. J. Delhalle, J.-M. André, Ch. Demanet, J.-L. Brédas, *Chem. Phys. Lett.* **54**, 186 (1978)
27. J. Delhalle, L. Piela, J.-L. Brédas, J.-M. André, *Phys. Rev. B* **22**, 6254 (1980)
28. Y.C. Zheng, J. Almlöf, *Chem. Phys. Lett.* **214**, 397 (1993)
29. Š. Varga, *Phys. Rev. B* **71**, 073103 (2005)