Density inversion method for local basis sets without potential auxiliary functions: inverting densities from RDMFT

S. Bousiadi[1,2], N. I. Gidopoulos[3], N. N. Lathiotakis[1]

1. Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48,116 35 Athens, Greece
2. Section of Condensed Matter Physics, National and Kapodistrian University of Athens,Panepistimioupolis,GR-157 84 Athens, Greece
3. Department of Physics, Durham University, South Road, Durham DH1 3LE, United Kingdom

The density inversion is a method for obtaining the Kohn-Sham potential that corresponds to a given electronic density ρ_t. It is a useful tool, because it can help to evaluate the quality of new functionals, but also give us an insight about how exact Kohn Sham potentials for different systems look. Although there exist other density inversion methods [1-3], it is difficult to use one systematically. The present method [4] is based on the minimization of the Coulomb energy of the difference of a non-interacting N electron system (ρ_u) and the target density (ρ_t):

$$U[\rho_u - \rho_t] = \frac{1}{2}\iint dr dr' \frac{[\rho_u(r) - \rho_t(r)][\rho_u(r') - \rho_t(r')]}{|r - r'|}$$

In our method, an important quantity is the screening density ρ_{scr}. The screening density can be thought of as the effective charge density that repels each Kohn-Sham electron. The algorithm constructed corrects the screening density in every step of the computational procedure by $\varepsilon(\rho_u(r) - \rho_t(r))$. Compared with other inversion methods, the present one has the advantage that in every iteration the screening charge (integral of the screening density) is constant and equal to N-1, where N is the number of electrons, which is property of the exact KS system. This property ensures the correct asymptotic behavior of the potential. Our method is a refinement of the work of Timothy J. Callow et. al [5]. More specifically, the density is expanded in products of the orbital basis elements, leading to better computational performance, and avoiding the necessity of an additional auxiliary basis for the expansion of the screening density. We applied our method to invert densities originating from both local (LDA) and nonlocal potentials such as CAS-SCF, HF but also from RDMFT. We have applied the method to densities obtained from functionals such as BBC3, ML, Power and PNOF-5. This method provides the opportunity to obtain a single particle spectrum, which is not explicitly and uniquely defined in the case of RDMFT. IPs were obtained as the minus of the HOMO eigenvalue and compared with those obtained from the total energies of each method and experimentally. Finally, we plotted the exchange and correlation potentials for different densities and systems.

1. Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A. 1994 50, 2138.
2. Y. Wang and R. G. Parr, Phys. Rev.A 1993 47, R1591
3. Q. Wu and W. Yang,J. Chem. Phys. 2003. 118, 2498
4. S. Bousiadi S, N. Gidopoulos , N.N Lathiotakis . Physical Chemistry Chemical Physics. 2022;24(32):19279-86.
5. T. J. Callow, N. N. Lathiotakis, N. I. Gidopoulos. J. Chem. Phys. 2020, 152, 164114