



## Reduced density matrix functional theory: An *ab-initio* approach describing strong (and weak) correlations

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Recently, reduced density matrix functional theory (RDMFT) has appeared as an alternative approach to handle complex systems. It has shown great potential for improving upon DFT results for finite systems [1] as well as extended systems [2, 3]. RDMFT uses the one-body reduced density matrix (1-RDM),  $\gamma$ , as the basic variable [4]. This quantity, for the ground state, is determined through the minimization of the total energy functional, under the constraint that  $\gamma$  is ensemble  $N$ -representable. The total energy as a functional of  $\gamma$  can be expressed as (atomic units are used throughout)

$$E_v[\gamma] = \int d^3r \int d^3r' \delta(\mathbf{r} - \mathbf{r}') \left[ -\frac{\nabla^2}{2} \right] \gamma(\mathbf{r}, \mathbf{r}') + \int d^3r v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\gamma], \quad (1)$$

where,  $\rho(\mathbf{r})$  —the electron density— is the diagonal of the 1-RDM and  $v(\mathbf{r})$  is the external potential. The first two terms in Eq. (1) are the kinetic and external potential energies. The electron-electron interaction can be cast in the last two terms, the first being the Coulomb repulsion energy and  $E_{xc}$  the exchange-correlation (xc) energy functional. In principle, Gilbert's [4] generalization of the Hohenberg-Kohn theorem to the 1-RDM guarantees the existence of a functional  $E_v[\gamma]$  whose minimum yields the exact  $\gamma$  and the exact ground-state energy of the systems characterized by the external potential  $v(\mathbf{r})$ . In practice, however, the xc energy is an unknown functional of the 1-RDM and needs to be approximated. In the past years, a plethora of approximate functionals, based on the original functional of Müller [5], have been introduced. An assessment of the relative performance of these functionals [6–8] for a large set of atoms and molecules reveals that the so called BBC3 [9] and PNOF0 [10] and power [3] functionals yield results for molecular systems, with an accuracy comparable to the MP2 method (as demonstrated in Fig. 1).

As for the extended systems the real challenge for any *ab-initio* theory is the prediction of

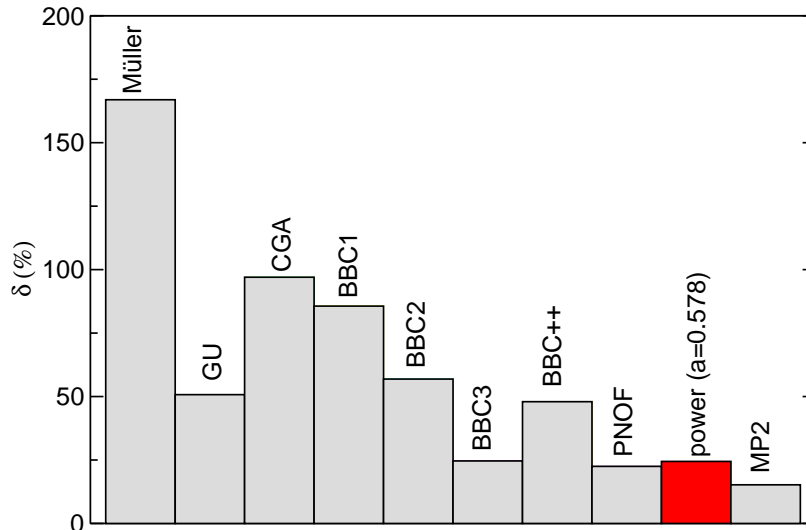


FIG. 1: Percentage deviation of the correlation energy, obtained using various functionals within RDMFT, from the exact CCSD(T) results [11].

an insulating state for the strongly correlated materials in the absence of any magnetic order –one of the most dramatic failures of the usual local/semi-local density approximations to the exchange-correlation (xc) functional of density functional theory (DFT) is the incorrect prediction of a metallic ground state for the strongly correlated Mott insulators, of which transition metal oxides (TMOs) may be considered as prototypical. For some TMOs (NiO and MnO) spin polarized calculations do show a very small band gap (up to 95% smaller than experiments) but only *as the result of AFM ordering*, however all TMOs are found to be metallic in a spin unpolarized treatment. On the other hand, it is well known experimentally that these materials are insulating in nature even at elevated temperatures (much above the Néel temperature). In our recent work we have shown that RDMFT not only predicts accurate gaps for conventional semiconductors, but also demonstrates insulating behavior for Mott-type insulators in the absence of any long range magnetic order [3]. This clearly points towards the ability of RDMFT to capture physics well beyond the reach of most modern day ground-state methods.

Despite this success the effectiveness of RDMFT as a ground state theory has been seriously hampered by the absence of a technique for the determination of spectral information. The reason for this lies in the fact that unlike DFT, RDMFT does not result in a set of single particle Kohn-Sham like equations. Although the value of the band gap itself can be determined from the chemical potential, which shows a discontinuity at integer particle

numbers [12, 13], no other spectral information is directly accessible for comparison with experiments like (inverse)photo emission spectroscopy. However, recently this impediment has been removed, in our recent work we propose a method for calculating the spectrum. Using this approach the spectra of a set of TMOs are determined (see Fig. 2). In all cases we find good agreement with experimental data [14].

In Fig. 2 is also present the site and angular momentum projected spectral density. The electronic gap, as expected, always occurs between lower and upper Hubbard bands dominated by transition metal  $d$ -states. As a validation of our method for the calculation of spectra we may compare the features of the projected spectral density, and in particular the ordering in energy of the  $t_{2g}$  and  $e_g$  states, with well-established *ab-initio* many-body techniques such as dynamical mean field theory and the  $GW$  method [15, 16]. In all cases we find excellent agreement, signaling that the method we present here yields an accurate description of the detailed features of the spectral density.

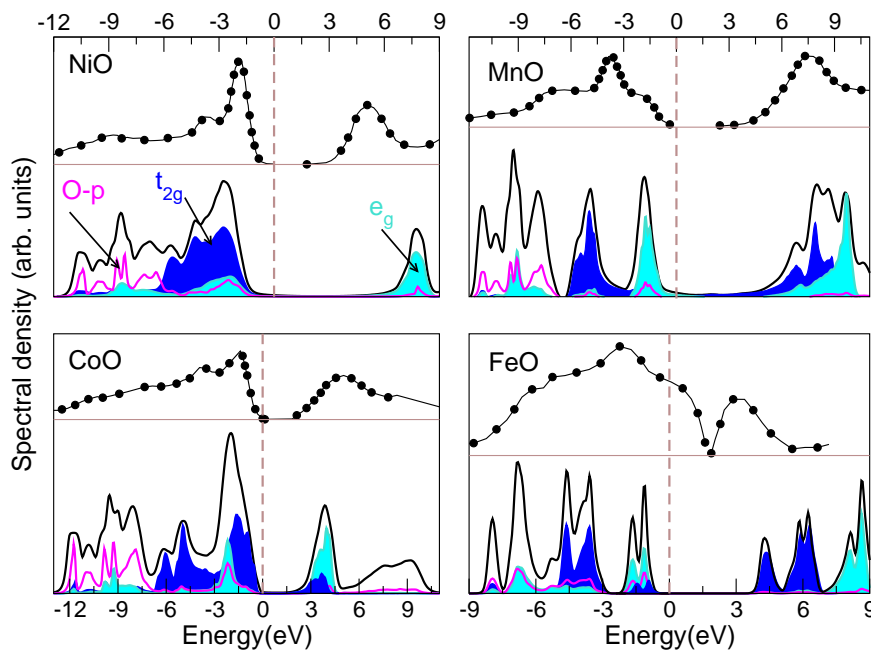


FIG. 2: Spectral density for the TMOs in presence of AFM order. Site and angular momentum projected spectral density are also presented for transition metal  $e_g$  and  $t_{2g}$  states and Oxygen- $p$  states. In addition XPS and BIS spectra (shifted up for clarity) are presented for comparison.

This opens up many future possibilities, such as the study of High  $T_C$  superconductors in their under-doped Mott insulating phase. It should also, hopefully, stimulate efforts to develop the theory formally, including a temperature dependent and magnetic extension of

RDMFT and functionals within RDMFT.

External co-workers on this project: N.N. Lathiotakis and N. Helbig

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