COMPARISON OF DENSITY FUNCTIONAL APPROXIMATIONS IN THE JELLIUM AND STABILIZED JELLIUM MODELS FOR METALS CLUSTERS

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We calculated the exchange, correlation and total energies of clusters of alkali metals with N= 1 - 150 atoms in the spherical jellium and stabilized jellium models. The calculations were made using the Kohn-Sham method with exchange and correlation energies evaluated in the Meta-Generalized Gradient Approximation (MGGA), proposed by J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, in the Generalized Gradient Approximation (GGA) of J. P. Perdew, K. Burke and M. Ernzerhof, and Local Density Approximation (LDA).
We evaluated the relative deviations of MGGA and GGA energies with respect to LDA. Both exchange and correlation energies of MGGA and GGA are higher than the LDA and become closer to this as the cluster size increases. On the other hand, the GGA and MGGA correlation energies, which are almost identical, are lower than LDA. The deviations of GGA and MGGA exchange-correlation energies with respect to LDA are smaller than those of the exchange and correlation energies separately. This pattern is valid for jellium as well as for stabilized jellium.
For clusters with 18 - 20 atoms we have compared our jellium results with Variational and Diffusion Monte-Carlo results. Errors of LDA for exchange and correlation tend to cancel so that the total exchange-correlation energy is close to the Monte-Carlo results. Similar cancellations occur with GGA and MGGA.
We also examined the validity of liquid drop model for the various density functional approaches.

1 Introduction

In Density Functional Theory, the Kohn-Sham self-consistent method allows to obtain solutions for the many-body problem where the only approximation is that made for the exchange and correlation energy functionals. In the Local Density Approximation (LDA) the exchange-correlation energy is

$$E_{xc}^{LDA}([n_\uparrow, n_\downarrow]) = \int d^3r \; n(r) \; e_{xc}^{i}(n_\uparrow(r), n_\downarrow(r)) \tag{1}$$

where the valence electron density is $n=n_\downarrow+n_\uparrow$, with $n_\downarrow$ and $n_\uparrow$ the up and down spin densities. We took the Perdew-Wang formula[1]. For improving the exchange and correlation energies Generalized Gradient Aproximation (GGA) density functionals have been developed. One of the most used is GGA-PBE[2] which includes explicitly density gradients:

$$E_{xc}^{GGA}([n_\uparrow, n_\downarrow]) = \int d^3r \; n(r) \; f_{xc}(n_\uparrow(r), n_\downarrow(r), \nabla n_\downarrow, \nabla n_\uparrow) \tag{2}$$

Recently, J. P. Perdew *et al.*[3] have proposed a generalization of GGA-PBE called Meta-GGA-PKZB (MGGA-PKZB). The general form of such a MGGA is

$$E_{xc}^{MGGA}([n_\uparrow, n_\downarrow]) = \int d^3r \; n(r) \; f_{xc}(n_\uparrow(r), n_\downarrow(r), \nabla n_\downarrow, \nabla n_\uparrow, \tau_\uparrow, \tau_\downarrow) \tag{3}$$

It includes as input, besides the electronic densities and their gradients, the kinetic energy density

$$\tau_\sigma = \frac{1}{2} \sum_{\alpha}^{occup} |\nabla \psi_{\alpha\sigma}(r)|^2 \tag{4}$$

In the spherical jellium model of clusters, as in the stabilized jellium model (a modification of jellium which includes a constant potential inside the cluster), one only needs to solve the Kohn-Sham equation in the radial dimension.

2 Calculations

In LDA, the exchange-correlation potential results from a functional derivative of the exchange-correlation energy with respect to the density. The computational cost of self-consistent GGA is higher than that of LDA. But we may calculate the exchange and correlation energies of GGA using the LDA density. This *a posteriori* GGA (or post GGA) gives results which are quite close to self-consistent GGA results but in a time similar to that of a LDA calculation. The same strategy was used to calculate the MGGA energies.

We took $n_\downarrow = n_\uparrow = n/2$. This is appropriate for clusters with closed shells, like sodium with N=18 and 20 atoms.

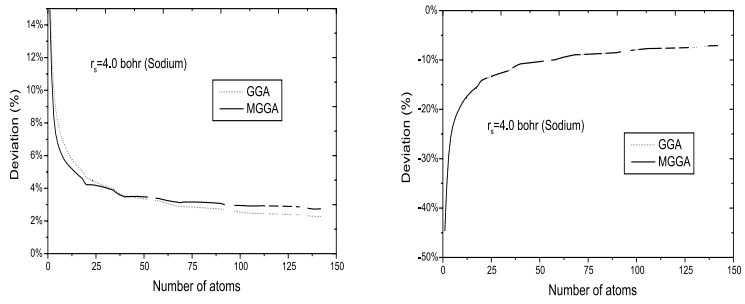

Figure 1. Relative deviations with respect to LDA of GGA and MGGA exchange (left) and correlation (right) energies for r_s=4.0 bohr (Na) in the jellium model.

3 Results

Figures 1-2 present exchange and correlation energies for a series of cluster (N $\leq$150) using the above mentioned GGA and MGGA (the reference is LDA). Both GGA and MGGA exchange and correlation energies approach the LDA case as the cluster size increases. However, MGGA is arriving at this limit slowly than GGA.

The results of density functional approaches were compared with corrected Variational Monte-Carlo (VMC) and Difusion Monte-Carlo (DMC) results from P. Ballone *et al.*[4]. We show results for Li, Na, and Cs with 18 - 20 atoms (Fig. 3). For each metal, the VMC correlation energies are corrected by a factor based on DMC for N=20. We have added the electrostatic energy of a uniform spherical positive charge to the VMC and DMC values of Ref.[4].

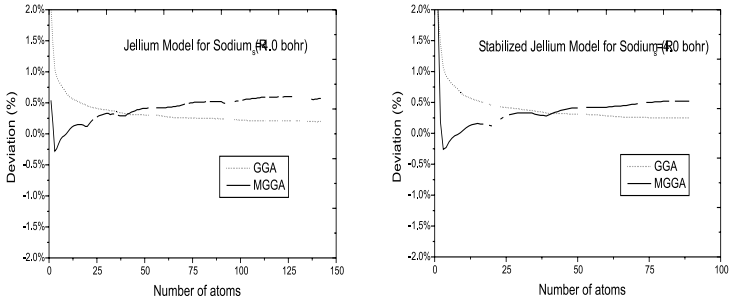

Figure 2. Relative deviations of GGA and MGGA exchange-correlation energies with respect to LDA for r_s=4.0 bohr (Na) in the jellium model (left) and stabilized jellium model (right).

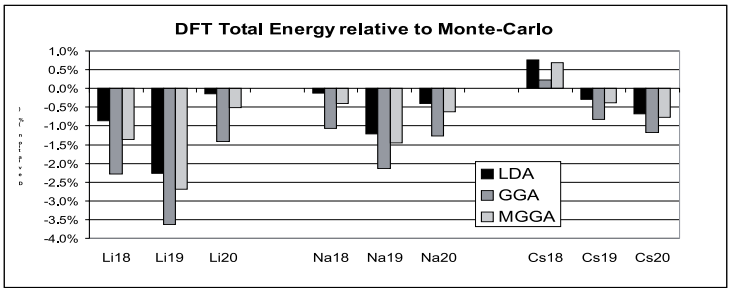

Figure 3. Deviations with respect to Monte-Carlo results (corrected VMC and DMC) for the total energy in various density functional approximations. Jellium densities of the clusters: r_s=3.25 bohr (Li), r_s=4.00 bohr (Na) , r_s=5.62 bohr (Cs).

Our results compared with the Monte-Carlo ones show a clear improvement of GGA and MGGA with respect to LDA exchange and correlation energies separately but not always of the sum of exchange and correlation. In fact, in spite of large

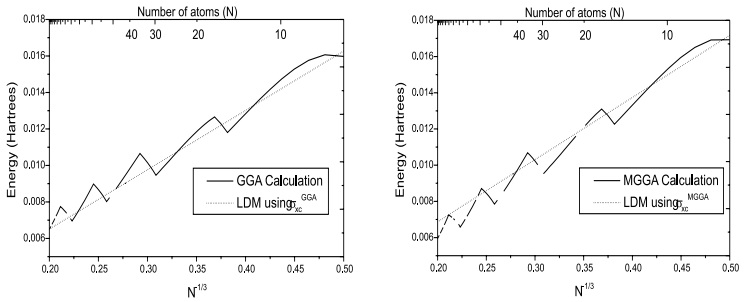

Figure 4. Comparison of the exchange-correlation energy per atom minus the correspondent energy of the uniform electron gas in GGA (left) and MGGA (right) with the Liquid Drop Model prediction. In the later, the surface tension was calculated using the semi-infinite jellium system. The contribution of curvature is neglected.

deviation of exchange and correlation energies in LDA the error in the total energy is remarkably small. Error cancellations occur since deviations of exchange and correlation energies have opposite signs. MGGA-PKZB improves on GGA-PBE for N=18-20 atoms.

Trends of the energy evolution with respect to cluster size are well described by the Liquid Drop Model (LDM), as Fig.4 shows. The main contribution to the difference between total energies and the bulk energies per atom is due to surface tension. Quantum shell effects are ignored in the LDM.

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