Ab initio molecular dynamics using density based energy functionals: application to ground state geometries of some small clusters.

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Abstract

The ground state geometries of some small clusters have been obtained via ab initio molecular dynamical simulations by employing density based energy functionals. The approximate kinetic energy functionals that have been employed are the standard Thomas-Fermi (T_{TF}) along with the Weizsacker correction T_W and a combination $F(N_e)T_{TF} + T_W$. It is shown that the functional involving $F(N_e)$ gives superior charge densities and bondlengths over the standard functional. Apart from dimers and trimers of Na, Mg, Al, Li, Si, equilibrium geometries for Li_nAl , n = 1, 8 and Al_{13} clusters have also been reported. For all the clusters investigated, the method yields the ground state geometries with the correct symmetries with bondlengths within 5% when compared with the corresponding results obtained via full orbital based Kohn-Sham method. The method is fast and a promising one to study the ground state geometries of large clusters.

PACS Numbers : 71.10, 31.20G, 02.70N, 36.40

I. INTRODUCTION

During the last few years the technique of first principles molecular dynamics (MD), initiated by Car and Parrinello (CP) [1,2], has emerged as a powerful tool for investigations of structural, electronic and thermodynamic properties of large scale systems. The standard implementation of this method which is based on density functional theory is via Kohn-Sham (KS) orbitals. Such orbital based algorithms scale as N_a^3 , N_a being the number of atoms in the system. Quite clearly, such methods turn out to be computationally expensive for system sizes over about 100 atoms [3]. Recently, approaches based on total energy functionals, which depend on charge density only or orbital free density functionals have been proposed [4–6]. These methods are based on approximate representation of kinetic energy (KE) functionals and offer an attractive alternative for investigating large scale systems. Since the method is orbital free i.e there are no wavefunctions to handle, there is no computationally expensive orthogonality constraint and the methods scale linearly with system size. In addition, these methods are shown to yield stable dynamics even with large timesteps, a highly desirable feature for molecular dynamics simulations.

It is clear that the utility of these methods is critically dependent on their ability to investigate the systems of interest with acceptable accuracy, at least for a class of physical properties. Madden and coworkers have investigated structural and thermodynamic properties of some simple metals with considerable success. For example, the dynamic structure factor of liquid Sodium and static structure factor, vacancy formation energy, free energies of point defects as well as phonon dispersion curves of Sodium [4,7] are well described by this method. The method has also been applied for ground state configurations of c-Si and H/Si (1 0 0) surface [6] and for geometries of some silicon clusters [8] and a good agreement has been found with experiments as well as with other calculations. However majority of the calculations reported so far have been performed on extended systems.

In the present work, we focus our attention on studying the ground state and energetically low lying structures of clusters, a field of current interest. Obviously, due to the approximate nature of the KE functionals the bondlengths and binding energies will not be obtained with the same level of accuracy as the KS orbital based methods. However, it is of considerable interest to examine whether such a method is capable of yielding the correct shapes (i.e the right symmetries) of clusters by employing Car-Parrinello simulated annealing methods. If desired the KS method can then be used to search the local minimum around structures obtained by Orbital Free Method (OFM) in 'quenching' mode. This can be a computationally tractable way to avoid the long and costly simulated annealing runs of the orbital based KS molecular dynamics.

Towards this end we have carried out a number of calculations on a variety of representative small clusters of simple metals. Specifically, we have investigated dimers and trimers of Na, Mg, Al, Li, Si, small clusters of Na_n , (n = 6, 8), Li_nAl , (n = 1, 8) and Al_{13} . These systems are representative of the small metal atom clusters of current interest and more accurate KS based results have been reported. Hence, it is possible to make an assessment of the present method by comparing the bondlengths and geometries with the reported ones.

The question of appropriate choice of kinetic energy functionals has been addressed by Smargiassi and Madden [9]. They have investigated a family of kinetic energy functionals which incorporate exact linear response properties. All such KE functionals are based on the Thomas Fermi (TF) and the Weizsacker correction term. Since our interest is in finite size systems, we have chosen to use simple KE functionals. These functionals have been previously used in the study of atoms and molecules. However, it must be mentioned that significant progress has been made towards improving the KE functionals notably by DePristo and Kress, Wang and Teter [10,11].

In the next section we briefly discuss the method, the KE functionals used and give the relevant numerical details. This is then followed by the results and discussion.

II. FORMALISM AND COMPUTATIONAL DETAILS

A. Total Energy Calculation

The total energy of a system of N_e interacting electrons and N_a atoms, according to the Hohenberg-Kohn theorem [12,13], can be uniquely expressed as a functional of the electron density $\rho(\mathbf{r})$ under an external potential due to the nuclear charges at coordinates \mathbf{R}_n ,

$$E\left[\rho, \{\mathbf{R}_n\}\right] = T[\rho] + E_{xc}[\rho] + E_c[\rho] + E_{ext}\left[\rho, \{\mathbf{R}_n\}\right] + E_{ii}\left(\{\mathbf{R}_n\}\right),\tag{1}$$

where E_{xc} is the exchange-correlation energy, E_c is the electron-electron Coulomb interaction energy. The electron-ion interaction energy E_{ext} is given by

$$E_{ext}[\rho, \{\mathbf{R}_n\}] = \int V(\mathbf{r})\rho(\mathbf{r})d^3r$$
(2)

where $V(\mathbf{r})$ is the external potential, usually taken to be a convenient pseudopotential [14]. The last term in Eq. (1), E_{ii} , denotes the ion-ion interaction energy. The first term in Eq. (1), the KE functional, is usually approximated as

$$T[\rho] = T_{TF}[\rho] + T_W[\rho] \tag{3}$$

where $T_{TF}[\rho]$ is the Thomas-Fermi term, exact in the limit of homogeneous density, and has the form

$$T_{TF}[\rho] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho(\mathbf{r})^{5/3} d^3r$$
(4)

and $T_W[\rho]$ is the gradient correction due to Weizsacker, given as

$$T_W[\rho] = \frac{\lambda}{8} \int \frac{\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r}) d^3 r}{\rho(\mathbf{r})}$$
(5)

which is believed to be the correct asymptotic behavior of $T[\rho]$ for rapidly varying densities. Instead of $\lambda = 1$, the original Weizsacker value, $\lambda = \frac{1}{9}$ and $\lambda = \frac{1}{5}$ [15] are also commonly used. It has been argued that for rapidly varying densities, which is the case for finite size clusters a more appropriate kinetic energy functional would be a following combination of these two terms [16]

$$T[\rho] = F(N_e)T_{TF}[\rho] + T_W[\rho]$$
(6)

where the factor $F(N_e)$ [17] is

$$F(N_e) = \left(1 - \frac{2}{N_e}\right) \left(1 - \frac{A_1}{N_e^{\frac{1}{3}}} + \frac{A_2}{N_e^{\frac{2}{3}}}\right)$$
(7)

with optimized parameter values $A_1 = 1.314$ and $A_2 = 0.0021$ [18]. This functional which includes the full contribution of the Weizsacker correction describes the response properties of the electron gas well. This functional has been used for investigating atoms and molecules with reasonable success.

We briefly describe our procedure, details of which can be found in [5]. The total energy of the system (Eq. (1)), is minimized for fixed ionic positions using the conjugate gradient method [19] which forms the starting point for molecular dynamics. The trajectories of ions and the fictitious electron dynamics are then simulated using Lagrange's equations of motion which are solved by Verlet algorithm [1]. The stability of CP dynamics has been discussed in [4] in the context of density based methods and timesteps of the order to 50 a.u. have been successfully used. We have verified that by appropriate adjustment of the fictitious electron mass the CP dynamics remains very stable for over 10000 iterations with a timestep of 40 a.u. in the present calculations of clusters. Typically, for free dynamics the grand total energy which is the sum of the kinetic energy of ions, kinetic energy of electrons and the potential energy of the system remains constant to within 10^{-5} a.u.

For the calculations of the ground state structures for dimers and trimers of Na, Mg, Al, Li and Si a periodically repeated unit cell of length 26 a.u. with a 54 × 54 × 54 mesh and timestep $\Delta t \sim 10$ to 20 a.u. was used. For the rest of the small clusters the calculations were done on a unit cell of length of 30 a.u with a 54 × 54 × 54 mesh. We have chosen to use the plane wave expansion on the entire fast fourier transform mesh without any truncation yielding the energy cutoff of 95 Rydberg. It must be mentioned that, due to the orbital free calculations the number of fast fourier transforms per iteration are constant irrespective of the number of electrons in the system. For clusters, the ground state configurations are obtained either by starting with different initial configurations and then quenching the structures or by dynamical simulated annealing where the cluster is heated to $300 - 350^{\circ}K$ and then cooled very slowly. In all the cases the stability of the final ground state configurations has been tested by reheating the clusters and allowing them to span the configuration space for a few thousand iterations and then cooling them to get the low energy configurations.

III. RESULTS AND DISCUSSION

In this section, we first discuss the results for the equilibrium bondlengths and binding energies of dimers and trimers of Na, Mg, Al, Li, Si along with their KS results. All the results presented here are obtained with energy convergence up to 10^{-13} for total energy minimization.

Table I shows the equilibrium bondlengths and binding energies for dimer and trimer systems using different kinetic energy functionals. These results have been compared with full nonlocal pseudopotential KS calculations. A few representative results using $\lambda = \frac{1}{5}$ have been given. It can be seen that for $\lambda = \frac{1}{5}$ the trend is similar to the $\lambda = \frac{1}{9}$ functional and there is no significant improvement in the results. Clearly, the results involving $F(N_e)$ functional show significant improvement over $\lambda = \frac{1}{9}$ (with the exception of Mg) and are in reasonable agreement with the bondlengths obtained by the KS method. The error in the bondlengths is around 10%. It is known that such methods based on approximate KE functionals are not expected to give accurate binding energies. One notable feature of the binding energy comparison is the considerable improvement by $F(N_e)$ over $\lambda = \frac{1}{9}$ (excepting again the case of Mg). The results for the Na, Li, Si trimer binding energies are not given because these are Jahn-Teller distorted isoscales triangles and the present method yields equilateral triangle geometries. Clearly, such density based methods are unable to reach the Jahn-Teller distorted geometries.

The quality of the charge densities obtained by this method can be gauged by comparing them with the KS charge density. In Fig. 1 we have plotted the self-consistent charge densities obtained using the functionals involving $F(N_e)$ (curve a) and $\lambda = \frac{1}{9}$ (curve b) with the KS charge density (curve c) for Al dimer along the axis joining the atoms. The ionic positions are marked by arrows on the plot. The KS charge density has been obtained using the identical pseudopotentials and the same cell size as in the case of OFM. Three prominent features can be observed.

- 1. Overall the $F(N_e)$ functional densities compare very well with the KS densities except at the origin where both the $F(N_e)$ and $\lambda = \frac{1}{9}$ self-consistent densities show overestimation.
- 2. At the atomic sites the $F(N_e)$ and KS based densities are very close and nonzero, whereas the $\lambda = \frac{1}{9}$ shows a disturbing feature of almost zero density.
- 3. At the peaks on either side of the origin, the KS and $F(N_e)$ charge densities again are close, but the charge density by $\lambda = \frac{1}{9}$ shows considerable overestimation.

In Fig. 2 we have plotted the superposed free atom charge density (0th iteration density) represented by the curve b and the self-consistent charge density for the functional involving $\lambda = \frac{1}{9}$ by the curve c and $F(N_e)$ by the curve a. The self consistent charge density obtained using $\lambda = \frac{1}{9}$ shows improvement only at the origin. Contrary to this the self consistent charge density using $F(N_e)$ shows a significant overall improvement, both at the origin and at the peaks on either side of the peak at the origin. To get an idea of the nature of the forces obtained by the OFM and KS dynamics, we have given the results for the vibrational frequencies for Na, Mg and Li dimers in Table 2. It is gratifying to note that the vibrational frequencies obtained by OFM method are in very good agreement with the KS ones.

To assess the utility and performance of this method, it has been applied to calculate the ground state geometries of a range of small clusters. We report here our calculations on heteronuclear clusters of $Li_nAl, n = 1, 8$ and a highly symmetric homonuclear cluster of Al_{13} and clusters of $Na_n, n = 6, 8$ using the $F(N_e)$ functional. The results are compared with the ones reported by KS method. The geometries of the heteronuclear Li_nAl clusters are shown in Fig. 3 and the bondlengths and symmetries in Table III. along with the KS results. Evidently, the present method not only reproduces the correct ground state geometry with bondlengths within 5% but also reproduces the two key features observed in the more accurate KS calculation [20].

- 1. The Li_nAl clusters for n < 3 are two-dimensional whereas from $n \ge 3$ the clusters become three-dimensional.
- 2. The Al atom gets trapped inside the Li atoms at n = 6.

It can also be noted that as the number of atoms in the cluster increases, the accuracy in the bondlengths appears to improve. However, for the case of Li_3Al and Li_8Al we get the ground structure configurations to be ideally symmetric rather than slightly Jahn Teller distorted geometries of the KS calculation.

We have also investigated the Al_{13} cluster since it shows an interesting icosahedral geometry. The calculations were performed in two different ways. First we started with a highly distorted icosahedron and applied the dynamical quenching to get the equilibrium geometry. In the second one, we started by placing the Al atoms at the fcc lattice points and heated the cluster to $300^{\circ}K$ and let the system span the configuration space for a few thousand iterations. This was then followed by a slow cooling schedule. It is very gratifying to note that in both the calculations the correct icosahedron is obtained with a bondlength of 4.88 a.u. as compared to the KS bondlength of 5.03 a.u. The error in the bondlengths being 3%. This strengthens our confidence in the ability of the method to reproduce the correct ground state geometries with acceptable bondlengths. In addition, we have also obtained the ground state geometries for Na₆, Na₈ and Na₂₀ and have verified that the geometries obtained are identical to those reported in [21], with the bondlengths differing by about 5%.

IV. CONCLUSION

In this work, we have presented the results obtained by using density based *ab initio* MD for a variety of small clusters and demonstrated that the method using approximate KE functionals is capable of yielding bondlengths within an accuracy of 5%. Our calculations indicate that the ground state geometries and symmetries of both homonuclear and heteronuclear clusters can be obtained within a reasonable accuracy and timesteps of the order of 40 a.u. can be used successfully for stable dynamics. The $F(N_e)$ functional is shown to give considerable improvement over standard $\lambda = \frac{1}{9}$ functional both in terms of charge densities and bondlengths and is thus recommended.

We believe the method to be a promising tool in the study of finite temperature and dynamical properties of clusters. So far, all the reported OFM calculations have been performed using local pseudopotentials only and it would be interesting to implement the nonlocal pseudopotentials and study the effect of nonlocality on the bonding and binding properties of such clusters. More work is required in this direction and the implementation of nonlocality is under consideration. It may be possible to expand the applications of OFM by incorporating the nonlocal pseudopotentials and by employing more accurate KE functionals. It is hoped that the problems of current interest in the field of clusters like fragmentation, dissociation, interaction between clusters, which may involve large number of atoms as well as more than one atomic species will be amenable by the present technique.

V. ACKNOWLEDGEMENTS

Partial financial assistance from the Department of Science and Technology (DST), Government of India and the Centre for Development of Advanced Computing (C-DAC), Pune is gratefully acknowledged. Two of us (V. S and D. N) acknowledge financial assistance from C-DAC. One of us (D. G. K.) acknowledges P. Madden for a number of fruitful discussions on the OFM. We also acknowledge K. Hermansson and L. Ojamoe for the MOVIEMOL animation program.

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| System | | Bondlength | ns | | | Binding en | lergies | |
|--------|-------------------------|-------------------------|----------|------------|-------------------------|-------------------------|----------|-------------------|
| | $\lambda = \frac{1}{9}$ | $\lambda = \frac{1}{5}$ | $F(N_e)$ | KS | $\lambda = \frac{1}{9}$ | $\lambda = \frac{1}{5}$ | $F(N_e)$ | KS |
| | | | | | | | | |
| Na_2 | 5.67 | - | 5.69 | 5.66^{a} | -0.116 | - | -0.867 | -0.71^{a} |
| Na_3 | 5.81 | 5.99 | 5.75 | 6.00^{b} | -0.207 | -0.281 | -1.286 | - |
| Mg_2 | 5.79 | - | 4.71 | 6.33^{c} | -0.195 | - | -1.432 | -0.115^{c} |
| Mg_3 | 5.94 | 5.81 | 4.87 | 5.93^{c} | -0.355 | -0.526 | -2.096 | -0.284^{c} |
| Al_2 | 5.74 | - | 4.14 | 4.66^{d} | -0.261 | - | -1.389 | -1.06^{d} |
| Al_3 | 5.88 | 5.57 | 4.32 | 4.74^{d} | -0.483 | -0.733 | -2.074 | -1.96^{d} |
| Li_2 | 5.87 | - | 5.51 | 5.15^{e} | -0.102 | - | -0.891 | - |
| Li_3 | 6.03 | 6.11 | 5.58 | 5.3^{b} | -0.182 | -0.256 | -1.311 | - |
| Si_2 | 5.35 | - | 3.74 | 4.29^{f} | -0.371 | - | -0.56 | -0.6 ^g |
| Si_3 | 5.50 | - | 3.92 | 4.10^{f} | -0.651 | - | -0.938 | - |

TABLE I. Comparison of the equilibrium bondlengths (in a.u) and binding energies (in eV/atom) using the different kinetic energy functionals with the KS self consistent method.

| ^a Reference | [21] | ^e our | own | KS | calcul | ations |
|------------------------|------|------------------|-----|----|--------|--------|
| | | | | | | |

^{*b*}Reference [22] f Reference [25]

^cReference [23] ^gReference [26]

 d Reference [24]

TABLE II. The vibrational frequencies (in cm^{-1}) of Na, Mg, Li dimer using the OFM and KS self consistent method.

| dimers | OFM | \mathbf{KS} |
|--------|-------|---------------|
| Na | 167.4 | 168 |
| Mg | 107.3 | 108.6 |
| Li | 273.7 | 311 |

TABLE III. The bondlengths between Li-AL of $Li_nAl, n = 1, 8$ using OFM compared with those obtained by KS method [20]. All the bondlengths are in a.u.

| system | OFM | KS | % error | Symmetry |
|----------|-----------------|-----------------|---------|----------------|
| LiAl | 4.77 | 5.35 | 10.8 | $C_{\infty v}$ |
| Li_2Al | 2×4.76 | 2×5.22 | 8.8 | C_{2v} |
| Li_3Al | 3×4.79 | 3×4.98 | 3.8 | C_{3v} |
| Li_4Al | 4×4.84 | 2×4.82 | 0.4 | C_{3v} |
| | | 2×4.89 | 1 | |
| Li_5Al | 4×4.84 | 4×4.74 | 2 | C_{4v} |
| | 4.95 | 5.13 | 3.3 | |
| Li_6Al | 6×4.79 | 6×4.58 | 4.5 | O_h |
| Li_7Al | 4.97 | 4.70 | 5.7 | C_{1h} |
| | 2×4.92 | 2×4.85 | 1.4 | |
| | 2×4.88 | 2×4.74 | 2.9 | |
| | 2×4.89 | 2×4.81 | 1.6 | |
| Li_8Al | 8×4.99 | 8×4.82 | 3.5 | D_{4d} |

Figure Captions

- 1. The self-consistent charge densities of Al dimer. Curve a represents the $F(N_e)$ functional charge density, curve b represents the $\lambda = \frac{1}{9}$ charge density and curve c denotes the charge density obtained using the KS method.
- 2. Comparison of self-consistent charge densities by the $F(N_e)$ (curve a) and $\lambda = \frac{1}{9}$ (curve c) functional for Al dimer with the superposed (0^{th} iteration) free Al atom charge density (curve b).
- 3. The ground state geometries of the Li_nAl clusters for n = 1, 8. The large sphere represents the Li atom and small sphere represents the Al atom.





