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## ***Ab initio* molecular dynamics via density based energy functionals**

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**Abstract.** The use of energy functionals based on charge density as the basic variable is advocated for *ab initio* molecular dynamics. It is demonstrated that the constraint of positivity of density can be incorporated easily by using the square root of the density for minimization of the energy functional. An *ad hoc* prescription for including non-local pseudopotentials for plane wave based calculations is proposed and is shown to yield improved results. Applications are reported for equilibrium geometries of small finite systems, viz. dimers and trimers of simple metal atoms like Na and Mg, which represent a rather stringent test for approximate kinetic energy functionals involved in such calculations.

### **1. Introduction**

First-principles density functional based molecular dynamics (DFMD), initiated by Car and Parrinello (CP) [1, 2], has become a powerful technique for *ab initio* investigations of a number of properties of clusters and extended systems [3]. This technique, which unifies the conventional density functional theory (DFT) with classical molecular dynamics, views the problem as that of total energy minimization involving electronic and ionic degrees of freedom. This is achieved via simulated annealing implemented through Lagrangian equations of motion, which are fictitious for electronic degrees of freedom and real for ionic coordinates. The method has also given impetus to the development of better and faster techniques for large-scale electronic structure calculations with fixed geometry, e.g. clusters involving a large number of atoms [4]. The applications based on the CP formalism fall into two broad categories:

- (1) *ab initio* prediction of ground state properties like equilibrium geometry and
- (2) finite-temperature properties obtained via trajectories of the system moving on the Born–Oppenheimer (BO) surface.

A majority of the applications belong to the first category. In spite of a number of technical advances like accelerated algorithms involving a real space approach [5], preconditioned conjugate gradient minimization methods [6] and analytically continued energy functionals [7], it is clear that the method becomes prohibitively expensive for large-scale calculations. Typically these algorithms scale as  $O(N_o^2 N_b)$  where  $N_o$  is the number of orbitals and  $N_b$  is the number of basis functions,  $N_o^2 N_b$  being the dominant cost of orthogonalization of electronic orbitals. In addition, for simple metal systems, a tricky problem of charge sloshing [6] has also been noticed which limits the time step that can be used in dynamics. Recently, there have been a few attempts towards obtaining linear scaling, e.g. a non-orthogonal localized basis formulation [8], finite-difference real space discretization coupled with the recursion method [9] and density matrix based formulation.

In the present work, following the Hohenberg–Kohn theorem [10, 11], we advocate a rather simple method in which the total energy functional is written in terms of density as the basic variable. Such an orbital free method (OFM) has been used by Pearson *et al* [12]. They have used this method for calculating equilibrium lattice separation, bulk modulus and vacancy formation energy of solid sodium. As pointed out in their work, the method scales linearly with the number of atoms  $N_a$  and is capable of treating large simulation time steps. The method has also been applied to the calculation of free energies of vacancies [13] and the ground state configuration of c-Si and H/Si(100) surfaces [14, 15]. The accuracy of this method hinges upon the correct description of the kinetic energy functional. Usually the kinetic energy functional is taken to be the Thomas–Fermi type with the appropriately scaled Weizsacker correction. This can be further improved by taking into account linear response properties, leading to the Perrot form [13]. However, there are a few points which must be critically examined. Firstly, the usual DFMD methods are implemented using first-principles pseudopotentials which are necessarily non-local. So far, the available orbital free formulation [12–15] uses local potentials only. Secondly, during the minimization process the positivity of the charge density  $\rho(\mathbf{r})$  must be strictly maintained. Thirdly, the accuracy of the results, at least so far as the bond lengths are concerned, which are crucial for ground state geometries and other structural properties, should be thoroughly assessed.

The present work is motivated by a desire to investigate these questions. This work includes the following.

(1) We propose an *ad hoc* prescription for incorporating the non-local contribution of the pseudopotential, which is missing from the earlier work.

(2) We use the square root of the density  $\sqrt{\rho(\mathbf{r})}$  as the basic variable to incorporate the positivity constraint on density. This constraint is essential because during unconstrained minimization, the electronic charge density  $\rho(\mathbf{r})$  may become negative, especially since the kinetic energy functionals are approximate. Indeed, in some cases we have observed this phenomenon.

(3) We present results of applications of this method to the equilibrium bond lengths of dimer and trimer systems. This would be a stringent test as compared to the applications to extended systems.

We believe that a combination of density based orbital free MD and Kohn–Sham (KS) orbital based MD may yield a cost effective way of performing geometry optimization for large clusters. This can be achieved by first obtaining approximate low-temperature structures by the present method which is  $O(N_a)$  and then performing full MD or a fast quench. As the kinetic energy functional improves, this way of geometry optimization should turn out to be a computationally tractable alternative for large clusters consisting of more than few hundred atoms. It may also be used for investigating the thermodynamic properties of large-scale systems where the conventional methods may be prohibitive in terms of computer time. The method will be most useful for simple metal systems provided it yields acceptable bond lengths. It is hoped that this kind of work will give impetus to formulating better kinetic energy functionals.

In the next section we give our formalism and computational details. In section 3 we present the results for  $\text{Na}_2$ ,  $\text{Mg}_2$  and  $\text{Mg}_3$  and compare them with full self-consistent KS calculations.

## 2. Formalism and computational details

### 2.1. Total energy calculation

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

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

where

$$T[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(\mathbf{r})^{5/3} d^3r + \frac{\lambda}{8} \int \frac{\nabla\rho(\mathbf{r}) \cdot \nabla\rho(\mathbf{r}) d^3r}{\rho(\mathbf{r})} \quad (2)$$

is the kinetic energy functional. The first term in this functional is the Thomas–Fermi term, exact in the limit of homogeneous density, and the second is the gradient correction due to Weizsacker. It has been pointed out that instead of  $\lambda = 1$  which is the original Weizsacker value,  $\lambda = \frac{1}{9}$  and other empirical values turn out to yield better results [16]. The second and the third term in (1) represent, respectively, the exchange–correlation energy in the usual local density approximation and the electron–electron Coulomb interaction energy. The next term

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

is the electron–ion interaction where  $V(\mathbf{r})$  is the external potential and the last term in equation (1),  $E_{\text{ii}}$ , denotes the ion–ion interaction energy.

The external potential is usually taken to be a convenient pseudopotential, and, in general, it is non-local. Let us recall that in the standard pseudopotential formulation [17] the non-local contribution to the electron–ion energy for an electron in the state  $\Psi(\mathbf{r})$  is given by

$$E_{\text{ni}}[\Psi] = \int \Psi(\mathbf{r}) V_{\text{ps},l}(\mathbf{r}) \hat{P}_l \Psi(\mathbf{r}) d^3r \quad (4)$$

where  $V_{\text{ps},l}(\mathbf{r})$  is the  $l$ -dependent part of the pseudopotential and  $\hat{P}_l$  is the angular momentum projection operator. In analogy, we suggest the following expression for non-local contribution to the total energy in terms of the square root of the density. Let

$$E_{\text{ni}}[\tilde{\rho}] = \int \tilde{\rho}(\mathbf{r}) V_{\text{ps},l}(\mathbf{r}) \hat{P}_l \tilde{\rho}(\mathbf{r}) d^3r \quad (5)$$

where

$$\tilde{\rho}(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}. \quad (6)$$

The exchange–correlation energy is calculated using the Ceperley–Alder exchange potential as interpolated by Perdew and Zunger [18]. Although in the present work we use a simple kinetic energy (KE) functional, improved KE functionals useful at least for simple metals have been reported. For example, Smargiassi and Madden [13] have investigated a family of KE functionals, with applications to Na and Al, giving accuracy comparable to that obtained by the KS method.

## 2.2. Dynamics

Typically the MD procedure proceeds via two steps. The first step is to obtain the ground state energy  $E$  and density  $\rho(\mathbf{r})$  for a fixed geometry, which could be done via CP dynamics performed on electronic degrees of freedom only. However, gradient based minimization techniques have also been found to be effective in locating the minimum of general functions and are known to have fast convergence [19]. We have applied the conjugate gradient (CG) algorithm [20–22] for minimizing the total energy functional for a fixed geometry configuration. In the standard CG algorithm the new charge density for the  $(k+1)$ th iteration is constructed by linearly combining the charge density  $\rho^k(\mathbf{r})$  and conjugate direction  $d^k(\mathbf{r})$  for the  $k$ th iteration as

$$\rho^{k+1}(\mathbf{r}) = \rho^k(\mathbf{r}) + \alpha^k d^k(\mathbf{r}) \quad (7)$$

where the search parameter  $\alpha^k > 0$  is chosen to minimize the functional  $E'(\alpha) = E[\rho^k + \alpha d^k]$  for a given  $\rho^k$  and  $d^k$ . It is well known that subsequent minimizations along the CG directions tend to introduce errors in the calculation due to finite precision. We have found it advantageous to restart the CG search after every few iterations with a steepest-descent direction. To incorporate the positivity constraint on density into the minimization procedure, we vary  $\bar{\rho}(\mathbf{r})$  (equation (6)) rather than  $\rho(\mathbf{r})$ , with equation (7) re-expressed in terms of  $\bar{\rho}(\mathbf{r})$ .

After performing minimization of charge density for fixed ionic positions to a desired degree of convergence, trajectories of ions and fictitious electron dynamics are simulated using Lagrange's equations of motion. To simulate the motion on the BO surface, we start with the Lagrangian defined by

$$L = K_e + K_a - E[\bar{\rho}, \{\mathbf{R}_n\}] \quad (8)$$

where

$$K_e = \mu \int \dot{\bar{\rho}}(\mathbf{r}) d^3r \quad (9)$$

and

$$K_a = \frac{1}{2} \sum_n M_n |\dot{\mathbf{R}}_n(t)|^2 \quad (10)$$

are the kinetic energy of electrons and the kinetic energy of the ions placed at  $\{\mathbf{R}_n\}$  respectively. The dot denotes the time derivative and  $\mu$  and  $M_n$  are respectively the fictitious mass of electrons and the mass of the  $n$ th atom. The fictitious mass of the electrons  $\mu$  is a parameter to model the classical motion of density analogous to atomic motion. The above Lagrangian leads to the following equations of motion:

$$\mu \ddot{\bar{\rho}}(\mathbf{r}, t) = -\frac{\delta E}{\delta \bar{\rho}(\mathbf{r}, t)} \quad (11)$$

$$M_n \ddot{\mathbf{R}}_n(t) = -\nabla_n E \quad (12)$$

for electrons and ions respectively, subject to the constraint

$$N_e = \int \bar{\rho}^2(\mathbf{r}) d^3r. \quad (13)$$

The dynamics being conservative the grand total energy  $E_{\text{GT}}$  is a conserved quantity of motion. Thus,

$$E_{\text{GT}} = E_e + E_a + E[\tilde{\rho}, \{\mathbf{R}_n\}] \quad (14)$$

is the sum of the fictitious kinetic energy of electrons, kinetic energy of ions and total energy of electrons. The equations of motion (11) and (12) are solved by discretizing time with a finite time step  $\Delta t$  using the Verlet algorithm [1]. It may be noted that large time steps are required for large simulation times which are essential for obtaining good thermodynamic averages. However, there are two limiting factors, the first being numerical accuracy due to the Verlet algorithm (second order in  $\Delta t$ ) and the second due to the coupled nature of the electron-ion system. In the context of OFMD the stability of CP dynamics has been discussed [12]. The grand total energy is the parameter used to monitor and judge the quality of DFMD numerical simulations. The greatest advantage of using density as the variational parameter is that the constraint of orthonogonality of wavefunctions can be done away with. This saves a considerable amount of computation, thus making the dynamics fast. An alternative to the CP algorithm for dynamical simulations of ionic systems has been suggested by Payne *et al* [6]. In this method the electronic degrees of freedom are relaxed to the instantaneous ground state at the new ionic coordinates. We have used this CGMD procedure along with the density predictor method [3] for dynamical simulations. The density in successive time steps is constructed using the first-order density predictor as

$$\tilde{\rho}'(\{\mathbf{R}_n(t+1)\}) = \tilde{\rho}(\{\mathbf{R}_n(t)\}) + [\tilde{\rho}(\{\mathbf{R}_n(t)\}) - \tilde{\rho}(\{\mathbf{R}_n(t-1)\})] \quad (15)$$

where  $\tilde{\rho}'$  denotes a trial density which is then used for further minimization. This reduces the number of CG minimization steps by a factor of two (typically two or three CG steps have been found to be sufficient for convergence).

The calculations for  $\text{Na}_2$ ,  $\text{Mg}_2$  and  $\text{Mg}_3$  have been performed on a periodically repeated unit cell of length 35 au with a  $48 \times 48 \times 48$  mesh. The square root charge density is expanded in terms of plane waves as

$$\tilde{\rho}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{\rho}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (16)$$

CG dynamics involves the calculation of the first derivatives of energies with respect to  $\tilde{\rho}(\mathbf{r})$ . The electrostatic energy, the gradient correction to the kinetic energy and the non-local energy and their respective derivatives were calculated in Fourier space and then transformed to  $\mathbf{r}$  space. The MD calculations were performed in the conventional CP technique and the conjugate gradient CP technique. Local calculations were conveniently performed in the  $\mathbf{r}$  space. The energy cut-off used for local calculations was 30 Rydbergs and that for non-local energy calculations 10 Rydbergs. The dimer dynamics with the conjugate gradient CP technique is quite stable with one CG step after adjusting the density by the predictor method for a time step of 10 au and  $\mu = 600$  au. Calculations with a time step of 50 au required four CG steps for the trajectories to remain on the BO surface.

### 3. Results and discussion

In this section, we present our results for the bond lengths of  $\text{Na}_2$ ,  $\text{Mg}_2$ ,  $\text{Mg}_3$  and compare them with those obtained via conventional *ab initio* MD. We have performed fixed geometry

minimization as well as simulated annealing MD. All the results presented here are obtained with energy convergence up to  $10^{-13}$  for total energy minimization.

The pseudopotentials used in the calculation are generated using the scheme of Bachelet *et al* [23]. In practice, these pseudopotentials are decomposed into two parts as

$$V_{ps}(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{l=0}^2 V_l(\mathbf{r}) \hat{P}_l. \quad (17)$$

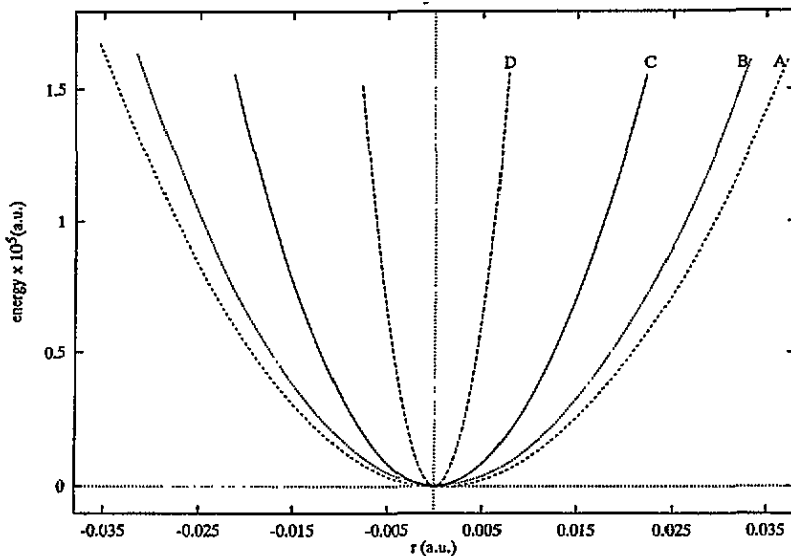
In our calculations, the local potential is taken as the sum of the first term which is  $l$  independent and the  $l = 0$  contribution from the second term. For the non-local calculation the full  $l$ -dependent potential is used. Identical potentials are used for the KS calculations. It may be noted that for simple metal atoms considered here the effect of non-locality is small and semi-empirical local potentials [12, 24] have been used successfully. However, for other systems the full non-local contribution is significant.

**Table 1.** Equilibrium bond length obtained via OFM local formulation (column 2) and OFM non-local formulation (column 3) compared with those of the KS self-consistent method (column 4) (all values in atomic units).

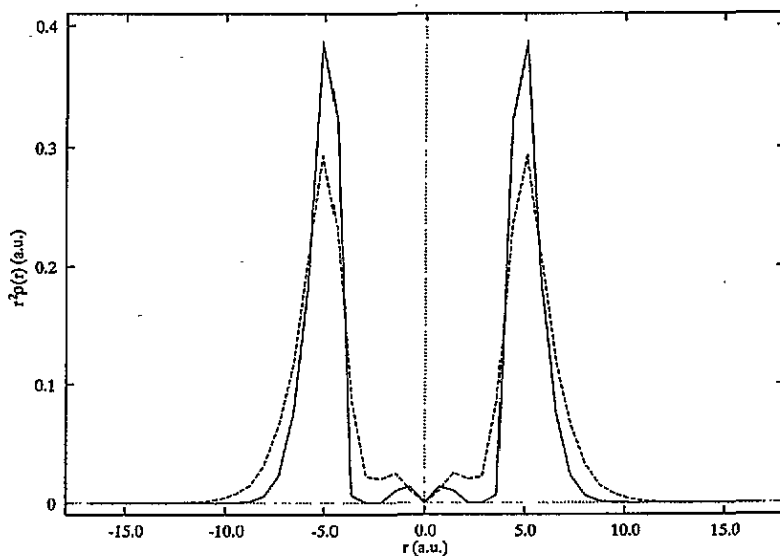
System	OFM local	OFM non-local	KS non-local
Na <sub>2</sub>	5.34	5.62	5.68
Mg <sub>2</sub>	5.35	6.32	6.26
Mg <sub>3</sub>	5.44	5.88	5.82

Table 1 shows the comparison of bond lengths via the OFM with local and non-local pseudopotentials and the KS self-consistent formulation. It is gratifying to note that the maximum error in the bond length with the non-local pseudopotential is of the order of 2%. It can be seen that non-locality improves the bond lengths considerably. However, this is at the cost of additional operations which go as  $N_a \times N_b$ .

In order to understand the total energy behaviour using OFM and also the effect of non-locality, we have plotted the total energy of Mg<sub>2</sub> as a function of interatomic separation in figure 1. The curve labelled A corresponds to the KS local results, B corresponds to the KS non-local and C and D represent the corresponding results obtained by the present method. The energy and the distances are measured with respect to the equilibrium quantities obtained by respective calculations. It can be seen that although the magnitude of changes is rather small, the effect of non-locality is somewhat drastic in the OFM. This leads to a faster approach to equilibrium with the inclusion of non-locality. However, it also shows a worrisome feature, namely, the effect of non-locality in the OFM is considerably more as compared to the full KS calculation. This indicates that although non-locality improves the equilibrium separation the vibrational frequencies would be significantly different from the KS results. Clearly this is an undesirable feature. To assess the quality of the charge density obtained via the OFM, we have plotted it in figure 2 along with that due to the KS method. As can be seen, there is an overall agreement in the nature of the density curve. The OF density is overestimated in the region away from the atomic site and underestimated at the atomic site. This is understandable due to the inexact formulation of kinetic energy functionals. However, the long-range behaviour is identical in the two cases. The variation of total energy  $E$  (continuous line) and  $E_{GT}$  (dashed line) with a time step of 10 au during the free MD simulation run for Mg<sub>2</sub> is shown in figure 3, indicating stable conservative dynamics. Identical behaviour has been seen with a higher time step  $\Delta t \sim 50$  au. The behaviour of the



**Figure 1.** The behaviour of total energy of  $\text{Mg}_2$  near equilibrium separation as a function of distance. All distances and energies are measured with respect to their corresponding equilibrium values. Curve A: KS local, B: KS non-local, C: OFM local, D: OFM non-local.



**Figure 2.** Charge density  $r^2\rho(r)$  along the symmetry axis for  $\text{Mg}_2$ . The dashed line corresponds to the KS result and the continuous line represents the OFM result.

total electronic energy is periodic, with the minimum occurring at the equilibrium separation in each oscillation. It may be mentioned that the Lagrangian dynamics (CP technique) is much faster and our results for a time step  $\Delta t \sim 20$  au are more or less identical to the CG dynamics results.



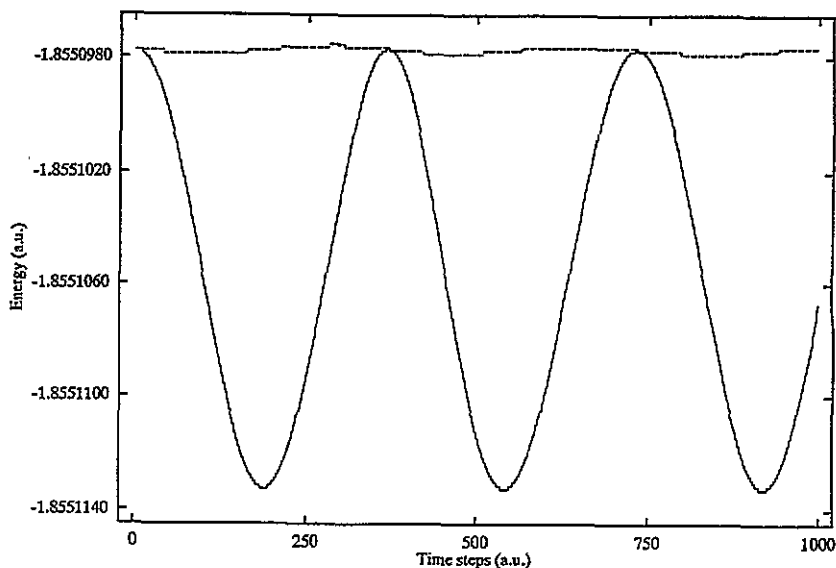


Figure 3. Time evolution of the total energy  $E$  (solid line) and grand total energy  $E_{GT}$  (dashed line) of  $Mg_2$  during a 1000-step free OFM MD run with a time step of 10 au.

#### 4. Conclusion

In this work we have presented a fast but approximate density based *ab initio* MD and demonstrated that the bond lengths for dimers and trimers are obtained to within an accuracy of 2% for non-local and  $\sim 10\%$  for local calculations. We have shown that the CG technique in conjugation with a simple density predictor method allows us to use large time steps for dynamics. The fixed-geometry minimization using CG can be obtained to a high degree of accuracy within less than 200 iterations. Yet another alternative to incorporate the positivity constraint is by constraining variation of density during the minimization (equation (7)) by restricting  $\alpha^k$  to an appropriate range [22]. Our preliminary investigation indicates that this technique is much faster compared to the square root density minimization. This is understandable, because it is well known that CG works best for quadratic and near-quadratic functionals, and the degree of non-linearity of the energy functional is reduced if expressed in terms of  $\rho$  rather than  $\tilde{\rho}$ .

The present calculations were performed on an i860 based workstation giving the performance  $\sim 5$  MFLOPS. One CP iteration for  $Mg_3$  using the OFM took a few seconds whereas the KS calculation took about 60 s. Since the OFM algorithm scales linearly with the system size it should be possible to handle a few hundred atoms per unit cell systems on standard workstations ( $\sim 30\text{--}40$  MFLOPS). We believe the present results on small systems to be a stringent test and the method to be a viable alternative for calculating finite-temperature properties of systems involving a large number of atoms.

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