Ab initio molecular dynamics via density based energy functionals

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Abstract

The use of energy functionals based on 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 square root density for minimization of the energy functional. An *ad hoc* prescription for including nonlocal 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.

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I. INTRODUCTION

First principle density functional based molecular dynamics (DF-MD), 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 Langrangian equations of motion, which are fictituous 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 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 Born-Oppenheimer (BO) surface.

A majority of the applications belong to the first category. Inspite of a number of technical advances like accelerated algorithms involving 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 timestep 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 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. The method has also been applied to the calculation of free energies of vacancies [13]. As pointed out in their work, at least for simple metallic systems the method scales linearly with the number of atoms N_a and is capable of treating large simulation timesteps. 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 DF-MD methods are implemented using first principles pseudopotentials which are necessarily nonlocal. So far, the available orbital free formulation [12,13] 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 bondlengths 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. In this work,

1. We propose an *ad hoc* prescription for incorporating the nonlocal contribution of the pseudopotential, which is missing from the earlier work.

2. We use square root density $\sqrt{\rho(\mathbf{r})}$ as the basic variable to incorporate the positivity constraint on density.

3. We present results of applications of this method to the equilibrium bondlengths 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 for 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 bondlengths. 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 III we present the results for Na_2, Mg_2 and Mg_3 and compare them with full self consistent KS calculations.

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, 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 $\mathbf{R}_n$.

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

where

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

is the kinetic energy functional. The first term in this functional is the Thomas-Fermi term, exact in the limit of homogenous 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 [14]. The exchange-correlation energy in the usual local density approximation is given by

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho)d^3r \tag{3}$$

where $\varepsilon_{xc}[\rho]$ denotes the exchange and correlation energy per particle of a uniform electron gas of density ρ.

$$E_c[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' \tag{4}$$

is the electron-electron Coulomb interaction and

$$E_{ext}\big[\rho, \{\mathbf{R}_n\}\big] = \int V(\mathbf{r})\rho(\mathbf{r})d^3r \tag{5}$$

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

The external potential is usually taken to be a convenient pseudopotential, and in general, it is nonlocal. Let us recall that in the standard pseudopotential formulation [15] the nonlocal contribution to the electron-ion energy for an electron in the state $\Psi(\mathbf{r})$ is given by

$$E_{nl}[\Psi] = \int \Psi(\mathbf{r})V_{ps,l}(\mathbf{r})\widehat{P_l}\Psi(\mathbf{r})d^3r \tag{6}$$

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

$$E_{nl}[\tilde\rho] = \int \tilde\rho(\mathbf{r})V_{ps,l}(\mathbf{r})\widehat{P_l}\tilde\rho(\mathbf{r})d^3r \tag{7}$$

where

$$\tilde\rho(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}. \tag{8}$$

The exchange-correlation energy is calculated using the Ceperley-Alder exchange potential as interpolated by Perdew-Zunger [16]. Although in the present work we use a simple

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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 comparable accuracy as obtained by KS method.

B. 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 [17]. We have applied the conjugate gradient (CG) algorithm [18–20] for minimizing the total energy functional for a fixed geometry configuration. Thus, starting with a trial $\mathbf{r}$-space charge density ρ^0, the CG algorithm proceeds as follows: the new charge density for the $k + 1^{th}$ iteration is constructed by linearly combining the charge density $\rho^k(\mathbf{r})$ and direction $d^k(\mathbf{r})$ for the kth iteration as

$$\rho^{k+1}(\mathbf{r}) = \rho^k(\mathbf{r}) + \alpha^k d^k(\mathbf{r}) \tag{9}$$

The initial search direction is taken to be the steepest descent direction

$$d^0(\mathbf{r}) = -g^0(\mathbf{r}), \tag{10}$$

and successive conjugate directions $d^k(\mathbf{r})$ are defined as

$$d^k(\mathbf{r}) = -g^k(\mathbf{r}) + \beta^k d^{k-1}(\mathbf{r}), \tag{11}$$

where

$$g^k(\mathbf{r}) = \frac{\delta E[\rho^k]}{\delta \rho^k(\mathbf{r})} \tag{12}$$

and

$$\beta^k = \frac{g^k \cdot g^k}{g^{k-1} \cdot g^{k-1}}. \tag{13}$$

The search parameter $\alpha^k > 0$ is chosen to minimize the functional $E'(\alpha) = E[\rho^k + \alpha d^k]$ for a given ρ^k and d^k. In the present case, we perform this line minimization numerically, using Brent's method [18], and we notice that it does not turn out to be very expensive (about 7 function evaluations to locate an α^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 $\tilde{\rho}(\mathbf{r})$ (Eq. (8)) rather than $\rho(\mathbf{r})$, with Eq. (9)-(12) reexpressed in terms of $\tilde{\rho}(\mathbf{r})$.

After performing minimization to a desired degree of convergence, trajectories of ions and fictitious electron dynamics are simulated using Langrage's equations of motion with Verlet algorithm. To simulate the motion on the BO surface, we start with the Lagrangian defined by

$$L = K_e + K_a - E\Big[\tilde{\rho}, \{\mathbf{R}_n\}\Big] \tag{14}$$

where

$$K_e = \mu \int \dot{\tilde{\rho}}(\mathbf{r}) d^3 r \tag{15}$$

and

$$K_a = \frac{1}{2} \sum_n M_n |\dot{R}_n(t)|^2 \tag{16}$$

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

$$\mu\ddot{\tilde{\rho}}(\mathbf{r}, t) = -\frac{\delta E}{\delta\tilde{\rho}(\mathbf{r}, t)} \tag{17}$$

$$M_n\ddot{\mathbf{R}}_n(t) = -\nabla_n E \tag{18}$$

for electrons and ions respectively, subject to the constraint

$$N_e = \int \tilde{\rho}^2(\mathbf{r})d^3r. \tag{19}$$

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

$$E_{GT} = E_e + E_a + E\Big[\tilde{\rho}, \{\mathbf{R}_n\}\Big] \tag{20}$$

is the sum of the fictitious kinetic energy of electrons, kinetic energy of ions and total energy of electrons. The grand total energy is the parameter used to monitor and judge the quality of DF-MD 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 considerable amount of computation, thus making the dynamics fast. An alternative to 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 CG-MD procedure along with the density predictor method [3] for dynamical simulations. The density in successive timesteps is constructed using the first order density predictor as

$$\tilde{\rho}\prime\Big(\{\mathbf{R}_n(t+1)\}\Big) = \tilde{\rho}\Big(\{\mathbf{R}_n(t)\}\Big) + \Big[\tilde{\rho}\Big(\{\mathbf{R}_n(t)\}\Big) - \tilde{\rho}\Big(\{\mathbf{R}_n(t-1)\}\Big)\Big] \tag{21}$$

where $\tilde{\rho}\prime$ denotes a trial density which is then used for further minimization. This reduces the number of CG minimization steps by a factor of 2 (typically 2 or 3 CG steps have been found to be sufficient for convergence).

The calculations for Na_2, Mg_2 and Mg_3 have been performed on a periodically repeated unit cell of length 35 a.u. with a $48 \times 48 \times 48$ mesh. The square root charge density is expanded in terms of plane waves as

$$\tilde{\rho}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{\rho}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}. \tag{22}$$

CG dynamics involves the calculation of the first derivatives of energies with respect to $\tilde{\rho}(\mathbf{r})$. The electrostatic energy, gradient correction to the kinetic energy and the nonlocal 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 conjugate gradient CP technique. Local calculations were conveniently performed in the $\mathbf{r}$-space. The energy cutoff used for local calculations was 30 Rydbergs and that for nonlocal energy calculations 10 Rydbergs. The dimer dynamics with conjugate gradient CP technique is quite stable with one CG step after adjusting the density by the predictor method for timestep of 10 a.u. and $\mu = 600$ a.u. Calculations with a timestep of 50 a.u. required 4 CG steps for the trajectories to remain on the BO surface.

III. RESULTS AND DISCUSSION

In this section, we present our results for the bondlengths of Na_2, Mg_2, Mg_3 and compare them with that obtained via conventional *ab initio* MD. We have performed both fixed geometry minimization as well as simulated annealing MD. All the results presented here are obtained with energy convergence upto 10^{-13} for total energy minimization

Table I shows the comparison of bondlengths via the OFM with local and nonlocal pseudopotentials and KS self consistent formulation. It is gratifying to note that the maximum error in the bondlength with nonlocal pseudopotential is of the order of 2%. It can be seen that nonlocality improves the bondlengths 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 nonlocality, we have plotted the total energy as a function of interatomic separartion in Fig. 1. The curve labeled A corresponds to the KS local results, B corresponds to the KS nonlocal, 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 nonlocality is somewhat drastic in OFM. This leads to a faster approach to equilibrium with the inclusion of nonlocality. However, it also shows a worrisome feature, namely, the effect of nonlocality in the OFM is considerably more as compared to the full KS calculation. To assess the quality of the charge density obtained via the OFM, we have plotted it in Fig. 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 understandably due to the inexact formulation of kinetic energy functionals. However, the long range behaviour is identical in both the cases. The variation of total energy E (continuous line) and E_{GT} (dashed line) with time during the free MD simulation run for Mg_2 is shown in Fig. 3. It can be seen that the grand total energy E_{GT} is constant throughout the simulation to an order of 10^{-6}. These results have been obtained by CG-MD using density predictor method. We have observed that for the dimer case a much higher timestep ~ 50 a.u. also keeps the system on Born-Oppenheimer surface with a slight increase in the computational cost. It may be mentioned that the Langragian dynamics (CP Technique) is much faster and our results for a timestep ~ 20 are more or less identical with the CG dynamics results.

IV. CONCLUSION

In this work we have presented a fast but approximate density based *ab initio* MD and demonstrated that the bondlengths for dimers and trimers are obtained to within an accuracy of 2% for nonlocal 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 timesteps 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 (Eq. (9)) by restricting α^k to appropriate range [20]. 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 nonlinearity of the energy functional is reduced if expressed in terms of ρ rather than $\tilde{\rho}$.

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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TABLE I. Equilibrium bonglength obtained via OFM local formulation (column 2) and OFM nonlocal formualtion (column 3) compared with that of KS self consistent method (column 4) (all values in atomic units).

System	OFM local	OFM nonlocal	KS nonlocal
Na_2	5.34	5.62	5.68
Mg_2	5.35	6.32	6.26
Mg_3	5.44	5.88	5.82

FIGURES

FIG. 1. The behaviour of total energy 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 nonlocal, C: OFM local, D: OFM nonlocal.

FIG. 2. charge density $r^2\rho(\mathbf{r})$ along the symmetry axis for Mg_2. The dashed line corresponds to the KS result and the continuous line represents the OFM result.

FIG. 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 timestep of 10 a.u.