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# Ab initio molecular dynamics, a simple algorithm for charge extrapolation

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## Abstract

A new simple algorithm to extrapolate the electronic charge density in ab initio molecular dynamics runs is proposed. The self-consistent charge density is decomposed in two parts, the first part is the sum of the atomic charge densities, and the second is its difference with the latter. The charge at time  $t + dt$  is constructed using the sum of the atomic charges and a second order extrapolation on the charge difference. The scheme is tested on a 64 atom liquid iron simulation under Earth's core conditions. A comparison with a simple second order extrapolation of the whole charge density shows that the new algorithm is significantly faster. © 1999 Elsevier Science B.V. All rights reserved.

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Ab initio molecular dynamics (AIMD) is a powerful tool to explore the properties of matter at the microscopic level. The interaction between ions and electrons is treated fully quantum mechanically, and the ions are moved using the classical Newton equation of motion.

The first pioneering work in AIMD is the one of Car and Parrinello (CP) [1], who proposed an unified scheme to calculate ab initio forces on the ions and keep the electrons close to the Born–Oppenheimer surface while the atoms move. They introduced a Lagrangian containing the ionic and electronic degrees of freedom. A fictitious mass, much smaller than the ionic masses, is assigned to the electrons, and the equation of motion is integrated for electrons and ions together. Due to the difference in the masses, the electrons follow adiabatically the motion of the ions. For more de-

tails refer to the original paper and also, for example, to Refs. [2,3].

An alternative approach to AIMD is performed by explicitly minimizing the electronic free energy functional at each time step. This minimization is more expensive than a single CP step, however, one is not limited in the length of the time step by the electronic mass and therefore the cost of the step is compensated by the possibility of making longer time steps. Moreover, the electronic minimizations become less expensive than on the first step if one is able to provide a good guess for the charge density and/or the wave functions. This can be done using multi-linear extrapolation. Although this is straightforward to apply to the charge, some care is needed for the wave functions, since they may be multiplied by an arbitrary phase factor or ordered in different ways in two contiguous steps. The solution to this problem as been proposed by by Arias, Payne and Joannopoulos [4] and by Mead [5]. Essentially, be-

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fore the extrapolation is performed, the two subspaces  $\{\Psi_{n,k}(t)\}$  and  $\{\Psi_{n,k}(t-dt)\}$  are “aligned” so that  $\sum_{n,k} \|\Psi_{n,k}(t) - \Psi_{n,k}(t-dt)\|$  is minimum. Then, the wave functions at time step  $t+dt$  may be written as

$$\Psi_{n,k}(t+dt) = \Psi_{n,k}(t) + \alpha[\Psi_{n,k}(t) - \Psi_{n,k}(t-dt)] + \beta[\Psi_{n,k}(t-dt) - \Psi_{n,k}(t-2dt)] \quad (1)$$

and, analogously, the charge

$$\rho(t+dt) = \rho(t) + \alpha[\rho(t) - \rho(t-dt)] + \beta[\rho(t-dt) - \rho(t-2dt)]. \quad (2)$$

$\alpha$  and  $\beta$  are calculated as proposed in Ref. [4], i.e. so that  $\sum_i \|\mathbf{r}'_i - \mathbf{r}_i(t+dt)\|^2$  is minimum, where

$$\mathbf{r}'_i = \mathbf{r}_i(t) + \alpha[\mathbf{r}_i(t) - \mathbf{r}_i(t-dt)] + \beta[\mathbf{r}_i(t-dt) - \mathbf{r}_i(t-2dt)], \quad (3)$$

and the sum runs over all the atoms in the unit cell. In other words,  $\Psi_{n,k}(t+dt)$  and  $\rho(t+dt)$  are the best quadratic extrapolations for the set of positions  $\mathbf{r}'_i$ , which are therefore made as close as possible to  $\mathbf{r}_i(t+dt)$ . It is straightforward to see that

$$\alpha = \frac{b_1 a_{22} - b_2 a_{12}}{\det A}, \quad \beta = \frac{b_2 a_{11} - b_1 a_{21}}{\det A}, \quad (4)$$

where

$$\begin{aligned} a_{11} &= \sum_i |\mathbf{r}_i(t) - \mathbf{r}_i(t-dt)|^2, \\ a_{12} &= \sum_i [\mathbf{r}_i(t) - \mathbf{r}_i(t-dt)] \cdot [\mathbf{r}_i(t-dt) - \mathbf{r}_i(t-2dt)], \\ a_{22} &= \sum_i |\mathbf{r}_i(t-dt) - \mathbf{r}_i(t-2dt)|^2, \\ a_{21} &= a_{12}, \\ b_1 &= - \sum_i [\mathbf{r}_i(t) - \mathbf{r}_i(t+dt)] \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(t-dt)], \\ b_2 &= - \sum_i [\mathbf{r}_i(t) - \mathbf{r}_i(t+dt)] \cdot [\mathbf{r}_i(t-dt) - \mathbf{r}_i(t-2dt)], \end{aligned}$$

and the sums run over all the atoms in the unit cell.

The algorithm to extrapolate the charge density proposed in this report is based on the fact that for many

systems the charge density is mostly determined by the superposition of the atomic charge densities. Therefore, writing

$$\rho(t) = \rho_{\text{at}}(t) + \delta\rho(t), \quad (5)$$

where  $\rho(t)$  is the self-consistent charge density at time  $t$ , and  $\rho_{\text{at}}(t)$  is the sum of the atomic charge densities<sup>2</sup>; the charge at time  $t+dt$  is simply extrapolated in the following way:

$$\rho(t+dt) = \rho_{\text{at}}(t+dt) + \delta\rho(t+dt), \quad (6)$$

where

$$\delta\rho(t+dt) = \delta\rho(t) + \alpha[\delta\rho(t) - \delta\rho(t-dt)] + \beta[\delta\rho(t-dt) - \delta\rho(t-2dt)]. \quad (7)$$

The atomic charge density can be calculated exactly and cheaply, and the scheme proposed here above is straightforward to implement. It has to be noted that the key point of the algorithm is not the use of the atomic charge *alone*, although this is the main contribution to the total electronic charge. An extrapolation based only on the atomic charge, i.e.  $\rho(t+dt) = \rho(t) - \rho_{\text{at}}(t) + \rho_{\text{at}}(t+dt)$  is quite unsatisfactory, being more or less of the same quality (if not worse) than that obtained using Eq. (2). The crucial improvement is the combination of the atomic charge *and* the extrapolation of the difference  $\delta\rho$ , as described by Eqs. (5), (6) and (7).

A comparison between the scheme of Eq. (2) and that of Eq. (5) for a simulation of liquid iron at 5000 K and density  $\rho_{\text{ion}} = 13.3 \text{ g/cm}^3$  will be shown. These are probably the thermodynamic conditions of the Earth's core [6]. The number of iron atoms used is 64. For this calculations the parallel version of the VASP code, running on 64 processors of the Edinburgh Cray/T3D parallel machine, has been used. The calculations are performed using a plane-wave basis set. The electron-ion interaction is described by ultrasoft pseudo-potentials [7,8] and the minimization of the electronic free energy is performed using an efficient iterative matrix-diagonalization scheme [9]. The integration of the equation of motion is performed using the Verlet algorithm [10], using a time step

<sup>2</sup> The sum of the atomic charge densities,  $\rho_{\text{at}}(t)$ , is calculated imposing the appropriate boundary conditions. In the present case these are the periodic boundary conditions of the simulation cell.

of 1 fs. The temperature is controlled using a Nosé thermostat [11]. The total electronic free energy per atom is required to be self-consistent within  $1.5 \times 10^{-7}$  eV/atom, in order to keep the drift of the constant of motion less than 100 K/ps. At each time step the wave functions are quadratically extrapolated after a “subspace alignment” [4] and the electronic charge density is extrapolated as proposed in Eq. (6) or according to Eq. (2). In Fig. 1 the CPU time per time step for the two possible extrapolation schemes is displayed. The first part of the simulation has been done using the extrapolation scheme of Eq. (2), then the scheme of Eq. (6) has been introduced. The total length of the simulation is 1 ps, and it is only the final part of a longer simulation of  $\approx 7$  ps. Since each run is limited in length by imposed maximum CPU time limit, the total simulation is a concatenation of many short runs. The sharp peaks in the figure correspond to the first step of each run. The higher ones ( $\approx 300$  s) correspond to those runs where random starting wave functions have been used, the lower ( $\approx 200$  s) correspond to runs where the starting wave functions are read from a file written by the previous run, and for this reason the convergence is faster. It is easy to recognize the point of the simulation where the extrapolation of Eq. (2) has been substituted by the one of Eq. (6), this is at about 0.55 ps from the beginning. The average simulation time per step has gone from  $\approx 170$  to  $\approx 100$  s. Moreover, the charge extrapolation scheme only affects the self-consistent cycle, and not the force and stress tensor calculations, that took  $\approx 10$  and  $\approx 20$  s, respectively. The data shown in Fig. 1 are inclusive of force and stress tensor calculation too.

To summarize, a new simple algorithm to extrapolate the charge density in ab initio molecular dynamics runs has been presented. The charge at the next step is the sum of the atomic charge density and the extrapolation of the difference between the atomic and the self-consistent charge density. This extrapolation scheme has been tested on a 64 atom liquid iron simulation under Earth’s core conditions, the CPU time has been compared to that of simulation done with a simple quadratic extrapolation of the whole charge density. The new scheme results in a significant reduction of computer time.

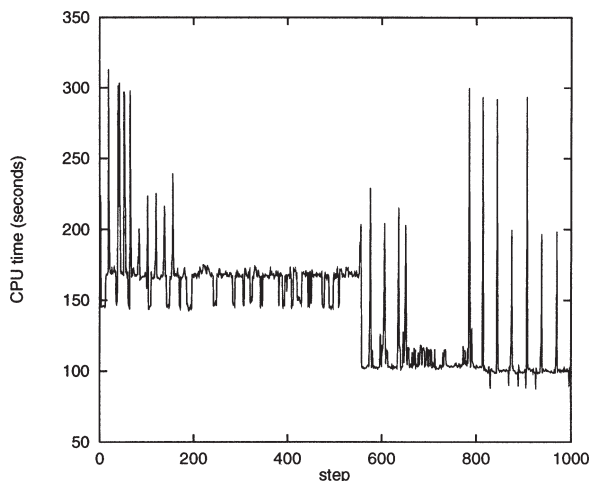


Fig. 1. CPU time per iteration as a function of the time step. The first 550 steps are performed using the extrapolation algorithm of Eq. (2), then the scheme proposed in Eq. (6) is introduced. The sharp peaks correspond the first iteration of each run (see text).

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