Implementing and evaluating a fictitious electron dynamics method for the calculation of electronic structure: Application to the Si(100) surface

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Abstract. A density matrix based fictitious electron dynamics method for calculating electronic structure has been implemented within a semi-empirical quantum chemistry environment. This method uses an equation of motion that implicitly ensures the idempotency constraint on the density matrix. Test calculations showed that this method has potential of being combined with simultaneous atomic dynamics, in analogy to the popular Car-Parrinello method. In addition, the sparsity of the density matrix and the sophisticated though flexible way of ensuring idempotency conservation while integrating the equation of motion creates the potential of developing a fast linear scaling method.

1. Introduction
Ab-initio quantum mechanical calculations are regularly used in electron structure calculations. Although very accurate, the size of the systems studied with these methods is typically restricted due to the unfavorable scaling of computational time with the number of atoms in the system [1] as well as the time required for calculating the large number of two-electron integrals. Due to this, there has been an upsurge of interest the last couple of years in the development of density matrix based methods which can improve this scaling. These methods are usually formulated within tight-binding or density functional theory and can achieve linear, or $O(N)$, scaling, with $N$ the number of atoms in the system, by taking advantage of the nearsightedness and consequent sparsity of the density matrix. Much larger systems can thus be studied using these methods than with conventional SCF calculations.

A density matrix based method employed within a semi-empirical quantum chemistry environment can, in principle, be used to study even larger systems than with tight-binding and density functional based methods, whilst still offering potential for $O(N)$ scaling. This is because semi-empirical methods, formulated within the same conceptual framework as the first principle methods, speed up calculations by neglecting some two-electron integrals and introducing empirical parameters for the remaining ones. Consequently, the system size that can be studied significantly increases although at the sacrifice of accuracy. With this in mind, a fictitious electron dynamics method for calculating electronic structure was developed [2,3] that uses an equation of motion for the density matrix. This equation implicitly contains the idempotency constraint on the density matrix and thus ensures a sophisticated though flexible way of enforcing constraints that are usually a very time consuming part of fictitious electron dynamics methods. The equation of motion was implemented within the semi-empirical quantum chemistry environment provided by the MOPAC software package [4]. This paper
focuses on the implementation of the method and presents test calculations carried out on a fictitious H₆-ring [4] and a Si₉H₁₂ cluster. The cluster represents atoms at and near a Si(100) surface. The potential of this method to study for example H-diffusion and eventually reaction dynamics on Si(100) and similar systems could thus be investigated.

2. Theory – Density matrix based fictitious electron dynamics
The heart of the fictitious electron dynamics method lies in the expression of an equation of motion for the one particle density matrix, \( P \) [2]. This equation is derived by considering the energy gradient with respect to \( P \) whilst enforcing idempotency, that is \( P^2 = P \), when changes in \( P \) are generated during a search for the ground state configuration. Based on this, the following equation of motion can be derived for \( P \):

\[
\dot{P} = (I - 2P)(\delta[F, P] + 2\dot{P}^2),
\]

with \( F \) the Fock matrix and \( b \) a constant related to an effective mass for the electronic degrees of freedom. The above equation is termed the fictitious electron dynamics equation of motion and it implicitly conserves the idempotency of the density matrix. However, numerical errors accumulate during integration and idempotency is not perfectly conserved. An criterion for the deviation from idempotency is given by the Euclidian norm of \( P^2 - P \), \( I_{tol} = \| P^2 - P \| \).

3. Implementation of the fictitious electron dynamics equations of motion
Equation 1 was implemented within the semi-empirical quantum chemistry environment provided by the MOPAC software package [4] which was used to calculate the Fock matrix and electronic energy. The integration of the equation of motion was done with the velocity Verlet algorithm [5]:

\[
P(t + \delta t) = P(t) + \delta t \dot{P}(t) + \frac{1}{2} \delta t^2 (I - 2P(t))(\delta[F(t), P(t)] + 2\dot{P}(t)^2).
\]

McWeeny purification [6] improved the idempotency conservation of the density matrix in the presence of accumulative numerical errors causing a drift of the density matrix away from idempotency. The ground state can be obtained using a simulated annealing approach based on the above equation of motion. A program development and application interface was created between MATLAB and MOPAC. This is especially convenient for obtaining graphical representations of the results.

4. Results and Discussion
A fictitious H₆-ring [5] was used to study the role of the parameters in the simulated annealing approach towards energy convergence using the above equation of motion as well as to study the sensitivity of the rate of convergence to the initial conditions. The mentioned parameters are the fictitious mass parameter, \( b' = \frac{1}{2} b \delta t^2 \), and the idempotency tolerance, \( I_{tol} \).

The effect of \( I_{tol} \) on energy convergence for an arbitrary value of \( b' \) is shown in figure 1. Clearly, a too large idempotency tolerance results in an inaccurate description of the ground state which has, for the H₆-ring, an energy of -210.085 eV as obtained by an SCF calculation using MINDO/3 parameters [5]. An idempotency tolerance of \( 10^{-4} \) was found to be small enough to ensure the correct ground state energy.

The fictitious mass parameter, on the other hand, is linked to the time it takes to reach energy convergence. Figure 2 shows that an optimum value for \( b' \) for this test system is between 0.10 and 0.15. The accuracy to which a molecular dynamics algorithm integrates the equations of motion can conveniently be measured by monitoring the degree to which it preserves conservation of total energy. Often the speed of the calculations has to be sacrificed for accuracy. This is evident from figures 3 and 4 for two values of \( b' \). The graphs show the number of time steps before the total energy starts to drop below the initial total energy that is supposed to remain constant. The electronic energy is decreasing as the ground state is being approached. Clearly, \( b' = 10^{-6} \) is most efficient in conserving energy for hundreds of time steps. However, from figure 2 it is clear that this will result in a much
more time-consuming calculation than for $b' = 10^4$. It can be noted in passing that the equation of motion for the configuration matrix, $C$, where $P = CC^T$, which can be derived from equation (1), conserves energy better than equation (1).

It is important to note that initial values for $\hat{P}$ and $P$ are needed to start the integration procedure. The selection of these can have an effect on the energy convergence. Shown in figures 5 and 6 is the influence of randomly selected initial $\hat{P}$ and $P$ matrices. The randomly selected $\hat{P}$ does not change the time needed to reach energy convergence, however, there are situations where a randomly selected $P$ resulted in slower energy convergence. Such a matrix can be interpreted as one that represents a state close to an excited state and thus a local energy minimum in electron configuration space. Despite this, energy convergence still occurs, regardless of the choice for the initial $\hat{P}$ and $P$.

Lastly, the efficiency of the equation of motion for the density matrix to keep the calculated electronic state close to the ground state during changes in the atomic configuration was investigated. For this, a Si$_9$H$_{12}$ cluster was used. The cluster represents atoms at and near a Si(100) surface. The H-atom was moved across the cluster as indicated in figure 7, while the electronic state was advanced with a few fictitious time steps for each atomic step. The resulting electronic energy was compared with the energy obtained with a SCF MINDO/3 calculation using the MOPAC software package. Figure 8 shows that 3 fictitious electron dynamics time steps are sufficient to keep the electronic state close to the Born-Oppenheimer energy surface.
5. Conclusions
A density matrix based fictitious electron dynamics method for the calculation of electronic structure has been successfully implemented within the semi-empirical quantum chemistry environment supplied by the MOPAC software package. A sophisticated, though flexible, method for enforcing the idempotency constraints on the density matrix was introduced. This method is capable of keeping the calculated electronic state close to the ground state during the motion of an atom and thus shows potential towards combination with atomic dynamics, analogous to the Car-Parinello [7] method. The density matrix based nature of the method also offers potential towards $O(N)$ scaling by taking advantage of the sparsity of the density matrix.

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