

Spin eigenstate-dependent Hartree–Fock molecular dynamics

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For the first time we present a fully ab initio molecular dynamics scheme for the treatment of many-electron ground and excited electronic states at the Hartree–Fock level using traditional Gaussian basis sets. The method is designed to simulate dynamics with first principles forces and to find global potential energy minima. Our first test examples concern the dynamics of singlet and triplet Na_4 . We find this cluster to exhibit strongly state-dependent dynamical behaviour that would not be observed in classical simulations.

Atomic clusters represent an area of specific interest for experiment and theory [1]. Traditional methods to simulate their dynamics require a priori knowledge of their potential energy surfaces, therefore more or less refined model potentials are in widespread use. In recent years, however, increased computer power and new ideas have opened up the field for a group of ab initio dynamics methods which calculate the potential energy surface “on the fly”, i.e. simultaneously with the simulation of the nuclei dynamics.

The central ideas have been formulated in the literature several times, for example by Bendt and Zunger [2] in the framework of density functional theory (DFT), or by Head-Gordon and Pople [3] using Hartree–Fock theory in an orthogonalized basis for geometry optimizations, but still traditional methods were deemed more efficient. Car and Parrinello [4] (CP) pioneered the practical application of ab initio dynamics in the DFT framework to extended solids by treating changes in the wavefunction as classical mechanical motion in a parameter (e.g. coefficient) space and on the same footing as the nuclear motion.

With few exceptions (e.g., ref. [5]), typical applications^{#1} so far have focused on geometry optimization in conjunction with general optimization methods like conjugate gradient or simulated an-

nealing [8,9]. Additionally, most of them employ DFT with a plane wave basis set. This strategy has two distinct advantages: since the basis set does not depend on nuclear positions, integrals over basis functions need not be recomputed as the atoms move, and the Hellmann–Feynman forces that have been used in the CP algorithm are quite accurate (i.e. no “Pulay corrections” [10,11] are necessary).

All this is well suited for treatment of infinite solids; for clusters, however, there are inherent weaknesses of DFT and plane wave basis sets: the exchange–correlation potential is taken as that for a three-dimensionally infinite electron gas [12], which is unlikely to be a good first approximation to electrons in cluster or molecules. In order to describe the wavefunction cusps due to Coulomb potentials, a gigantic number of basis functions (typically [13] 25000–50000 plane waves) is necessary (this situation can be improved by pseudopotentials, which consequently are used very often). Since there are periodic boundary conditions linked with the plane wave basis, large unit cells are necessary to isolate clusters from each other, especially metal clusters with long wavefunction tails and extended transition metal s and p functions. Lastly but probably most importantly, DFT cannot properly calculate electronically excited states [14] (“spin-polarized” DFT wavefunctions are not eigenfunctions of spin) but rather is limited to calculating ground state properties.

^{#1} For a review see ref. [6] and for representative work, ref. [7].

There have been some promising examples using floating Gaussians: Pederson, Klein and Broughton [10] optimized DFT wavefunctions and calculated Hellmann–Feynman forces for Li_2 and the Ne atom, however without performing any dynamics. Sprik and Klein [15] used simulated annealing to optimize the wavefunction for one solvated electron and also propagate this wavefunction together with the solvent molecules. Tsou, Estrin and Singer [16] combined simulated annealing and conjugate gradient optimization to simultaneously optimize the geometry and wavefunction of a sodium atom in argon clusters; they follow several electronic states during their dynamics simulation, but again their model is essentially for one electron only. In another application [17], the same authors use a similar optimization strategy for two-electron systems with correlated floating Gaussians as an alternative to a CI treatment, but without any real dynamics.

Attempts to combine traditional Gaussian basis sets and Hartree–Fock theory into a similar *ab initio* molecular dynamics scheme have been rare. Some groups tried a semi-empirical treatment [18] for simulation of spectra and geometry optimization. Chacham and Mohallem [19] have used simulated annealing in the Hartree–Fock framework, but as their example is simply the helium atom, there is no geometry optimization or even forces – so this was just another way of solving for the wavefunction instead of using the Roothaan matrix diagonalization method. Independently and simultaneously with the present work, Field [20] has used full forces from Hartree–Fock wavefunctions for water and formamide to optimize their structures. An excited open shell singlet state was also studied at single points on the potential energy surface, but no dynamics were reported for either case.

Thus, we introduce a fully *ab initio* many-electron implementation of the CP method in a local Gaussian basis, well suited for cluster dynamics and geometry optimizations, for both ground and excited electronic states. We use standard Gaussian basis sets plus effective core potentials and marginally modified HF-SCF programs. As a first test of our procedure, we present here a model calculation of the short-time dynamics of singlet and triplet Na_4 clusters on the HF-SCF level.

With the molecular orbitals expanded in a Gaus-

sian basis, $\phi_i = \sum_{\mu} c_{\mu i} \chi_{\mu}$, the CP Lagrangian [4] can be written as

$$L = \sum_{\mu i} \frac{1}{2} m |\dot{c}_{\mu i}|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 - E(\{c_{\mu i}\}, \{R_I\}), \quad (1)$$

where m is the fictitious mass associated with the SCF coefficients and M_I are the nuclear masses. The first term represents the fictitious kinetic energy, the second term the nuclear kinetic energy, and the third term is the potential energy (which is a function of the SCF coefficients $c_{\mu i}$ and the nuclear coordinates R_I). The Lagrangian is subject to the orthonormality constraint on the orbitals

$$\sum_{\mu\nu} c_{\mu i} c_{\nu j} S_{\mu\nu} = \delta_{ij} \quad (2)$$

(where $S_{\mu\nu}$ is the overlap integral between the basis functions χ_{μ} and χ_{ν}). Eqs. (1) and (2) lead to the equations of motion

$$m \ddot{c}_{\mu i} = - \frac{\partial E}{\partial c_{\mu i}} + \sum_{j\nu} \lambda_{ij} c_{\nu j} S_{\mu\nu},$$

$$M_I \ddot{R}_I = - \nabla_I E, \quad (3)$$

where λ_{ij} are Lagrange multipliers associated with the constraint forces.

The equations of motion require the real and fictitious forces $F = -\partial E/\partial q$, where $q = c_{\mu i}, R_I$. Marginally modified standard electronic structure programs [21,22] are used to obtain the terms and matrices for Hellmann–Feynman and internuclear repulsion forces

$$\frac{\partial E}{\partial R_I}^{\text{Hel-Fey}} = \sum_i \sum_{\mu\nu} c_{\mu i} c_{\nu i} \langle \chi_{\mu} | -Z_I \frac{R_I - r}{|R_I - r|^3} | \chi_{\nu} \rangle$$

$$+ \frac{\partial V_{\text{NN}}}{\partial R_I} \quad (4)$$

and for the fictitious forces on the SCF coefficients,

$$\frac{\partial E}{\partial c_{\nu i}^n} = 2 \sum_{\mu} c_{\mu i}^n F_{\mu\nu}^n, \quad (5)$$

where $F_{\mu\nu}^n$ is an element of the Fock matrix for shell n in the atomic basis.

A simple Verlet algorithm [23], eq. (6), is employed to propagate q according to the above forces,

$$q(t + \Delta t) = 2q(t) - q(t - \Delta t) + (\Delta t)^2 F(t)/m. \quad (6)$$

The constraints on the SCF coefficients are applied

via the standard SHAKE procedure [24].

In order to gain speed, the integrals over atomic basis functions and the Hellmann–Feynman forces are not recalculated every time step. Tests in comparison with propagations updating integrals and forces at every step have shown that the nuclear motion suffers no loss in accuracy when the integrals are updated every fifth step and the forces are recalculated every tenth step with linear extrapolation in between. Since the accuracy of this particular scheme depends on the system, its momentary location on the potential energy surface and its temperature, the skip lengths should be decided upon automatically and dynamically according to a measure for the overall geometrical change to achieve a general scheme [25].

The length of the time step is optimized by checking total energy conservation in test runs with full forces. The optimized time step, here 5.0 atu ($1 \text{ atu} = 2.41888428 \times 10^{-17} \text{ s}$) or approximately 0.12 fs, conserves the total energy of the system with an error on the order of 5×10^{-6} hartree. In the actual propagations the total energy varies on the order of 3 mhartree over a period of 50 fs, which reflects solely the approximate nature of Hellmann–Feynman forces and is not an indicator for insufficient convergence of the finite difference propagation. The fictitious mass for the SCF coefficients is optimized such that the nuclear motion stays close to the limit of zero fictitious mass. Here we use a value of 300 au or approximately 0.16 amu (one order of magnitude more or less produces no visible change in nuclear motion in short test runs of 100 time steps). When there is no interest in reproducing a “physically real” trajectory, e.g., in a geometry optimization, a larger mass and therefore a larger time step can be used.

Both test cases, trajectories for the restricted Hartree–Fock (RHF) singlet Na_4 and the restricted open shell Hartree–Fock (ROHF) triplet Na_4 , were initiated from the same “distorted, elongated tetrahedron” geometry far away from any of the possible final geometries. The SCF coefficients should start from wavefunctions converged for two slightly different geometries corresponding to the initial nuclear velocity, but here for simplicity, all initial velocities are set to zero. In the course of the propagation, the wavefunction is reconverged every

500 steps, bringing the system back to the true Born–Oppenheimer potential energy surface. As a result of initiating the trajectories far away from equilibrium, both clusters heat up rapidly. Nevertheless, the whole system of nuclear coordinates and wavefunction parameters undergoes completely free dynamics. We did not find it necessary to drain kinetic energy from the wavefunction coefficient motion, as done by other authors (e.g. ref. [16]), since the fictitious kinetic energy of the coefficients was in the order of 10^{-6} hartree and therefore always less than 0.1 percent of the real kinetic energy of the nuclei (in contrast to Field’s case [20], where the fictitious kinetic energy is even dominant).

Fig. 1 shows the development of the nuclear geometries over a period of 0.273 ps in both our test cases. Very obviously, the dynamics are extremely state dependent: The singlet exhibits two shrinking “bond distances” (2–4 and 1–3); the triplet has one “bond” (2–4) shrinking and the other (1–3) expanding. The characteristic features of the wavefunction in both cases elucidate the reason for these differences: The doubly occupied HOMO of the singlet has one node, but is still bonding between two pairs of sodium atoms (1–3 and 2–4). Therefore the system can lower its electronic energy by pushing the sodium atoms inside these pairs together to their equilibrium distance and by pulling the pairs themselves away from the nodal plane (which diminishes the wavefunction gradient at the node and thus decreases the electronic kinetic energy). The singly occupied HOMO of the triplet is higher in energy and has to have one more node. By the same argument as above, this introduces a force which pushes the sodium atoms away from the nodal plane. Since the HOMO in this case is centered mainly upon one of the sodium atom pairs (1–3), these two atoms repel each other while the other pair (2–4) manages to stay close.

Thus these preliminary tests have shown that our method works correctly and produces physically reasonable results, especially that it is capable of giving electronic state-dependent dynamics which are unavailable in classical molecular dynamics simulations and in *ab initio* molecular dynamics employing DFT (as discussed above). A future publication [25] is scheduled to give all pertinent details, an extension to the generalized valence bond method, and

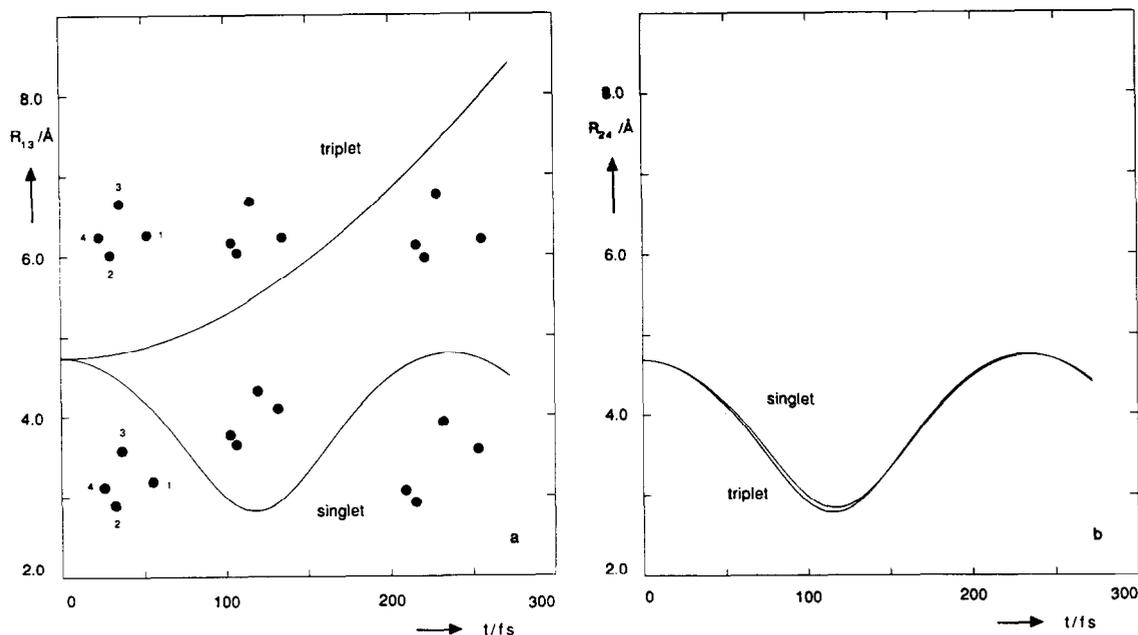


Fig. 1. Movement of the nuclei in singlet and triplet Na₄ propagation: (a) The distance R_{13} between nuclei 1 and 3 (in Å) behaves markedly different during the propagation time t (in fs). In the triplet (top), it increases monotonically, while in the singlet (bottom), these nuclei approach each other and then show the beginning of an anharmonic vibration around their equilibrium distance. (b) The distance between nuclei 2 and 4 as a function of time behave very similarly in the triplet and the singlet and closely resemble the behavior of R_{13} for the singlet case. The insets in (a) display projections of the full, three-dimensional, distorted tetrahedron geometry of the clusters at times $t=0.0, 0.11, 0.235$ ps. The orientation of the cluster is the same for the singlet and the triplet. The starting geometries are identical, with atoms 2 and 4 on a approximate perpendicular bisector of atoms 1 and 3. The temporal development of the cluster geometry again emphasizes the difference between the singlet and the triplet.

cooling schedules to exploit the ability of simulated annealing to find global energy minima.

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