Ab Initio Molecular Dynamics with Excited Electrons

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A method to do *ab initio* molecular dynamics suitable for metallic and electronically hot systems is described. It is based on a density functional which is costationary with the finite-temperature functional of Mermin, with state being included with possibly fractional occupation numbers. Optimization with respect to density only, rather than states and occupation numbers, is necessary. As an illustration, the method is used to calculate structure and dynamics in dense hot hydrogen.

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A few years ago Car and Parrinello (CP) [1] introduced a method to perform *ab initio* molecular-dynamics simulations based on density functional theory (DFT). In this approach the ionic and electronic degrees of freedom are treated on an equal footing through the introduction of a Lagrangian in which the dynamical variables include the electronic orbital coefficients. Such an approach has proved to be useful and stable in the simulation of chemically complex materials. In spite of its great success, the CP approach needs to be improved in many ways. First, it cannot treat in a practical way fractionally and/or thermally occupied states. Second, the integration for the CP equations of motion requires a time step which is dictated by the dynamics of the *fast* electronic degrees of freedom and which turns out to be rather small, particularly for small or even zero-gap systems such as metals. Similar problems are encountered when plane waves of high momentum are needed to expand the orbitals. The use of plane waves to expand the Kohn-Sham (KS) orbitals imposes the use of periodic boundary conditions. This makes the simulation of isolated and/or charged systems cumbersome [2]. Finally, because of the orthonormalization requirement of orbitals, the cost of a single iteration in the CP and derived algorithms scales like N^2M for large systems, where M is the basis set size and N the number of particles. In electronic optimization calculations this has to be multiplied by the number of iterations needed to achieve convergence, which depends on the nature and size of the system.

Recently there have been attempts by several groups to overcome these drawbacks. As a solution to the time step problem, Pearson, Smargiassi, and Madden [3] have shown that it can be substantially increased if the density, and not the orbitals, is used as the dynamical variable. This, however, they achieved at the expense of making an approximation to the kinetic energy functional. As a solution to the scaling problem, several authors [4] have proposed algorithms which scale more favorably than N^3, but again this more favorable scaling is achieved only at the expense of some approximations or assumptions.

Here we present an alternative formulation of density functional-based molecular dynamics which extends to interacting fermions the approach of Alavi and Frenkel [5] and which has a number of attractive features. First, it incorporates consistently the effects of thermal electronic excitations and fractionally occupied states. Second, the functional can be evaluated for any given electronic density in a strictly *NM* procedure and does not involve orthonormalization. Third, it can be implemented entirely on a real space grid. Fourth, it enables us in principle to do CP-like dynamics on the electronic density *without making any approximations to the kinetic energy.* Fifth, the efficiency in optimizing the functional is not greatly reduced in the case of metallic systems. We show below that this algorithm can be implemented in practice by studying dynamics in dense hydrogen both in molecular and metallic regimes.

We consider an energy functional which is the sum of the (Helmholtz) free energy of an electron gas of density $n(\mathbf{r})$ and ion-ion Coulomb energy (E_{II}):

$$\mathcal{F} = \Omega + \mu N + E_{II}, \tag{1}$$

where Ω is the grand potential for an interacting spin-$\frac{1}{2}$ Fermi gas within DFT,

$$\Omega[n(\mathbf{r}), R_I] = -\frac{2}{\beta}\ln\det\left(1 + e^{-\beta(\mathcal{H}-\mu)}\right) - \int d\mathbf{r}\, n(\mathbf{r})\left(\frac{\phi(\mathbf{r})}{2} + \frac{\delta\Omega_{\mathrm{xc}}}{\delta n(\mathbf{r})}\right) + \Omega_{\mathrm{xc}}. \tag{2}$$

Ω_{xc} is the finite-temperature exchange-correlation grand potential functional; $\phi(\mathbf{r})$ is the Hartree potential; $\beta = 1/k_BT_e$ is the electronic temperature parameter; $\mathcal{H}$ is the one-electron Hamiltonian $\mathcal{H} = -1/2\nabla^2 + V(\mathbf{r})$; and

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$V(\mathbf{r})$ is the effective density-dependent potential,

$$V(\mathbf{r}) = \sum_I V_{eI}(\mathbf{r} - R_I) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta \Omega_{\mathrm{xc}}}{\delta n(\mathbf{r})} . \quad (3)$$

In the limit of zero temperature the first term of Eq. (2) reduces to the band energy contribution and Ω_{xc} to the ground-state exchange-correlation energy (E_{xc}), such that in this limit $\mathcal{F}$ becomes the Harris energy functional [6]. Like this latter functional, $\mathcal{F}$ is explicitly defined for *any* density $n(\mathbf{r})$, but is clearly its generalization to finite T. Moreover, $\mathcal{F}$ shares the same *stationary* point as the exact finite-temperature functional proposed by Mermin [7]. This can be seen by noting the following property of Ω:

$$\frac{\delta \Omega}{\delta V(\mathbf{r})} = n^{(o)}(\mathbf{r}), \quad (4)$$

where $n^{(o)}$ is the output electronic density,

$$n^{(o)}(\mathbf{r}) \equiv \sum_i f_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}), \quad (5)$$

where f_i are the (thermal) Fermi-Dirac occupation numbers and ψ_i the one-electron eigenstates of $\mathcal{H}$ evaluated using $n(\mathbf{r})$. Equation (4), together with thermodynamic relation $(\partial \Omega / \partial \mu)_{n(\mathbf{r})} = -N$ which implicitly defines μ in terms of $n(\mathbf{r})$, can be used to compute the functional derivative of $\mathcal{F}$ with respect to $n(\mathbf{r})$:

$$\frac{\delta \mathcal{F}}{\delta n(\mathbf{r})} = \int d\mathbf{r}' \, [n^{(o)}(\mathbf{r}') - n(\mathbf{r}')] \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 \Omega_{\mathrm{xc}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right) . \quad (6)$$

The stationary point of $\mathcal{F}$ occurs when $n^{(o)} = n$, i.e., at self-consistency. But this is precisely the same condition required to minimize the Mermin functional, and therefore the two functionals share the same stationary point. However, unlike the latter functional, $\mathcal{F}$ can exhibit a saddle point at stationarity if the kernel of the integral (6) is not positive definite [8,9].

The evaluation of $\mathcal{F}$ can be done efficiently through use of the Trotter approximation. The full density matrix is expressed as a product of P high temperature matrices: $e^{-\beta \mathcal{H}} = (e^{-\beta \mathcal{H}/P})^P$, where P is a large integer, so that $\epsilon = \beta / P$ is small, and then the Trotter approximation is applied: $e^{-\epsilon(K+V)} = e^{-\epsilon V/2} e^{-\epsilon K} e^{-\epsilon V/2} + \mathcal{O}(\epsilon^3)$. Since the kinetic term is diagonal in reciprocal space and, for local forms of V, the potential term is diagonal in real space, the application of the propagator to a state could, in principle, be implemented in the manner of CP, i.e., using fast Fourier transform techniques. However, here we use the purely real space approach of Alavi and Frenkel [5]. A suitable discretized approximation to this high temperature propagator is the sparse matrix

$$\rho_{ij} = \begin{cases} \frac{1}{6} e^{-(\beta/2P)(V_i + V_j)}, & i, j \text{ nearest neighbors} \\ 0, & \text{otherwise}. \end{cases} \quad (7)$$

The value of P is related to β and the mesh spacing δ and is given in reduced units by $\beta / P = \delta^3 / 3$. [This mesh spacing also defines the energy cutoff (E_{cut}) in a reciprocal plane-wave description.] If required, periodic boundaries can be easily supplemented. The eigenvalues λ_i of ρ are related to the energy eigenvalues ϵ_i of $\mathcal{H}$ via $\epsilon_i = -(P/\beta) \ln \lambda_i + \mathcal{O}(k^4/P)$, where k is the wave vector associated with ϵ_i. Diagonalization of ρ_{ij} is efficiently performed using the Lanczos algorithm [10]. The number of Lanczos iterations required to obtain the N largest eigenvalues of the $M \times M$ matrix ρ (where M is proportional to N with a large constant of proportionality) was found to scale linearly with N, making the evaluation of $\mathcal{F}$ an $\mathcal{O}(NM)$ process to a good approximation.

The output density $n^{(o)}$ is expressed in terms of the eigenvectors of ρ (which are those of $\mathcal{H}$ apart from errors introduced by the Trotter factorization), as in Eq. (5). These eigenvectors are expressed in terms of the Lanczos vectors v_j as $\psi_i = \sum_i^{L_i} a_{ij} v_j$, where L_i is the number of Lanczos iterations required to converge the ith state. In a generic application of the Lanczos method $L_i \sim N$ so that the construction of $n^{(o)}$ is in principle an $\mathcal{O}(N^2 M)$ process. However, because of the preconditioning explained below, we found that for high-energy states (large i) $L_i \sim i$, whereas for the low-energy states (small i), L_i can be held essentially constant. This latter feature greatly reduces (but does not altogether eliminate) the prefactor of the asymptotic N^3 tail. The basis for the preconditioning is that, since $\lambda_i = e^{-\beta \epsilon_i / P}$, the gaps between all states $\epsilon_i < 0$ are exponentially *increased,* whereas those between $\epsilon_i > 0$ are exponentially *decreased.* Consequently, the rate of convergence of the Lanczos iteration, which is strongly dependent on the spacing of the eigenvalues [11], is extremely rapid for the low-lying states. Finally, this convergence can be further enhanced by choosing the starting vector of the iteration to be a weighted sum over the states of the previous self-consistency iteration, thereby ensuring substantial overlap with all desired states. In numerical tests, the overall scaling for systems sizes of up to 512 atoms was found to be $\mathcal{O}(N^{2.4})$, implying that the asymptotic limit has not been reached even for such large systems. It is possible to accelerate further the rate of convergence by considering the shifted matrix $\rho' = \rho + (1 - e^{-\beta \mu / P}) I$, which has the property that all states $\epsilon_i < \mu$ have $\lambda_i > 1$, while all $\epsilon_i > \mu$ have $\lambda_i < 1$. Consequently, any gap at μ will be amplified by raising ρ' to some convenient power.

For dynamical simulations two approaches can be adopted based either on optimization of the electronic density at every time step or on a Lagrangian formulation in which the density is dynamical. We concentrate here on the former approach; the latter requires special treatment owing to the saddle-point behavior of the functional and will be published elsewhere. The Hellmann-Feynman forces are easily obtained through differentiation of $\mathcal{F}$ with respect to the ionic coordinates, with no further computational effort. In addition, in contrast to the original CP method, the dynamics in the present scheme is isothermal rather than adiabatic. In the isothermal limit, transitions between electronically excited states are allowed, but there is no phase coherence between these states.

Calculations have been performed on hydrogen under conditions of high temperature and pressure. This system can exhibit metallic and/or molecular behavior. Calculations [12] exist for comparison. In addition, because of the absence of core electrons, use of a local potential suffices [13]. Ω_{xc} was treated within the local density approximation (LDA). Finite-temperature expressions for Ω_{xc} are available in the literature [14], but for the densities and temperatures of interest here, they are essentially independent of T. We used, instead, the standard zero-temperature results of Ceperley and Alder as parametrized by Perdew and Zunger [15]. At each time step, the stationary point of $\mathcal{F}$ was found by self-consistent diagonalization using the Anderson mixing scheme [16] for the density. The criterion for convergence in the forces on the ions was set to $\sum_I |F_I(n) - F_I(n-1)| < 10^{-5}$ for the nth iteration, which gave rise to an energy conservation in the integration of the equations of motion of approximately 1 part in 5000, using the Verlet algorithm and a time step of 20 a.u. (≈ 0.5 fs) (see Fig. 1). Typically approximately 10 iterations were needed to achieve convergence. Simulations on the hydrogen dimer yielded a bond length of 1.48 a.u. and a vibrational frequency of 4150 cm^{-1}, in agreement with CP simulations.

Systems consisting of 64 hydrogen atoms placed in a cubic box with periodic boundary conditions were studied at a range of densities [$r_s = 1.3, 1.5, 1.7$; $r_s = (3/4\pi\rho)^{1/3}$] and temperatures $700 < T < 10\,000$ K. The calculations were performed with a grid of size 24^3 (20 Ry) at $r_s = 1.3$ and with 36^3, 40^3 (32 Ry) at $r_s = 1.5, 1.7$. Three sets of simulations were performed. One with $T_e = 300$ K, which is rather cold and corresponds essentially to a adiabatic ground-state calculation, and two others with "hot" electrons at $T_e = 10\,000$ and $50\,000$ K. Two-temperature regimes such as the latter are encountered in the initial stages of radiatively heated plasmas, where thermal equilibration of ionic and electronic subsystems takes place over relatively long periods of time [17]. We discuss here only a part of the results to illustrate the method; full details will be published elsewhere. The ionic configurations were initially prepared in a randomized highly unstable diamond configuration and equilibrated over runs of 0.2 ps, during which the ions disordered. The initial data being discarded, the runs were continued for an additional 0.2 ps, during which thermal averages were computed.

The $T_e = 300$ K calculations yielded results in excellent agreement with the earlier simulations of Hohl *et al.* [12]. Pair-distribution functions are shown in Fig. 2. At $r_s = 1.3$ the dimeric structure of the H_2 molecule is almost completely absent. At $r_s = 1.5$, the pronounced first peak at 1.5 a.u. indicates a tendency for dimerization, though the unusually high minimum that follows implies that a large fraction of the dimers are either highly stretched or dissociated. The integrated number of ions up to this minimum is 1.4. Inspection of atomic trajectories reveals the presence of short-lived atomic species, whose collisions with the dimers lead frequently to reactive scattering. At $r_s = 1.7$ the ions are clearly paired, the

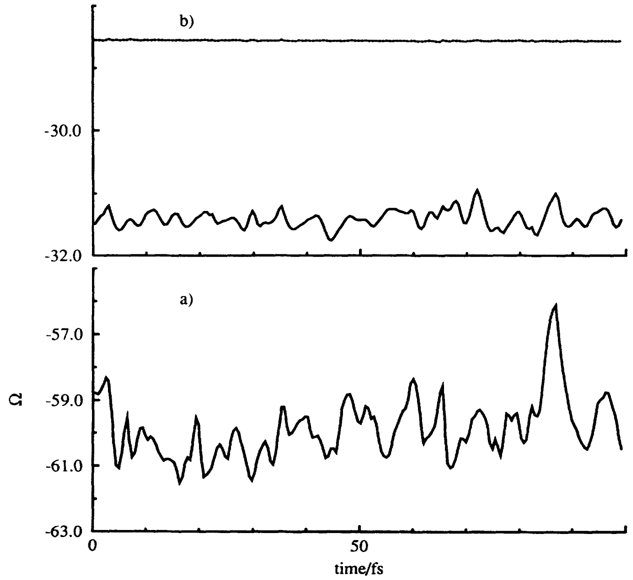

FIG. 1. Example of energy conservation during a microcanonical run. (a) Ω, (b) solid line: $\mathcal{F}$, dotted line: $\mathcal{F} + K$, where K is the ionic kinetic energy. All energies are in atomic units.

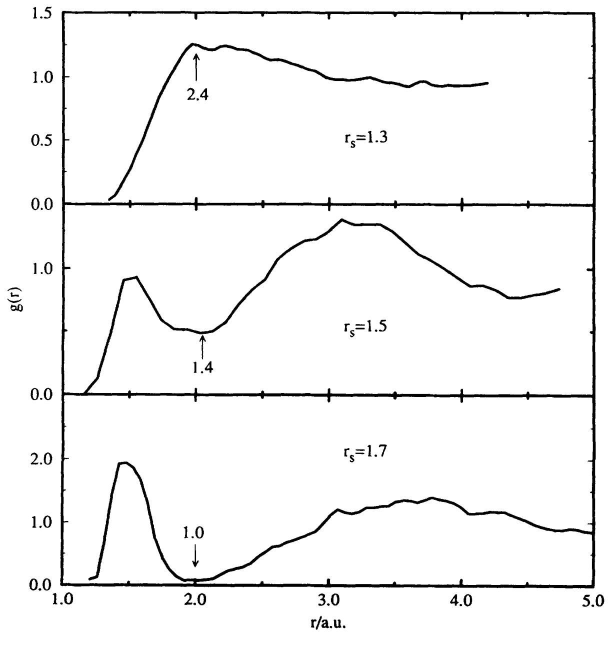

FIG. 2. Pair correlation functions with "cold" electrons ($T = 1000$ K).

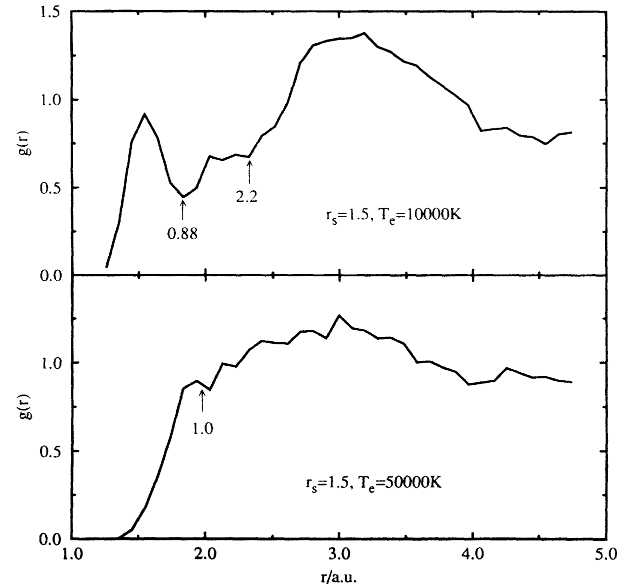

FIG. 3. Pair correlation functions with "hot" electrons (T = 700 K).

first peak of $g(r)$ integrating to 1. Figure 3 shows pair correlation functions for $r_s = 1.5$ at $T = 700$ K for two high electronic temperature runs. At $T_e = 10\,000$ K, the first broad peak narrows (and integrates to less than 1), while a small second peak appears at 2 a.u., possibly to indicate a larger number of longer-lived dissociated species. At $T_e = 50\,000$ K, the structure has dramatically changed. Almost all molecules have dissociated, and the first peak of the $g(r)$ has vanished.

In summary, we have described a method to do *ab initio* simulations at finite electronic temperatures in which the ground state approximation can be recovered in the suitable limit. The breakdown of the latter approximation is shown in the case of the hydrogen plasma in a two-temperature regime. The scaling properties and memory requirements of this method are more favorable than other presently available exact algorithms. Its extension to nonlocal potentials, as well as a Lagrangian formulation, is the subject of current studies.

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