

Nonholonomic Ab Initio Molecular Dynamics for Computational Materials Design

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ABSTRACT

A new nonholonomic Hamiltonian formulation of ab initio molecular dynamics avoids the limitations of Born-Oppenheimer, Car-Parrinello, and Ehrenfest methods, and offers important research opportunities in the application of simulation to nanocomposite materials design.

Keywords: molecular dynamics, ab initio methods, computational materials design

1 INTRODUCTION

Nanocomposites research attempts to design new materials with unique or optimized properties, by forming composites at the nanoscale. Previous work has demonstrated the ability to significantly modify the mechanical, electrical, magnetic, thermal, or chemical properties of various bulk materials by adding relatively small amounts of nanoparticles, nanorods, or nanotubes. Despite this success, the realization of dramatic improvements in engineered materials remains a difficult task. Understanding the thermal, mechanical, and chemical dynamics of fabrication processes is critical if the aforementioned potential is to be realized in macroscale devices. Example defense applications of current research interest include the development of new energetic materials, the development of high ampacity nanocomposite electrical conductions, and the development of sensitive and selective nanocomposite explosive sensors.

The majority of published research on nanocomposites has taken an experimental approach. Simulation can serve as a valuable adjunct to experiment, reducing the time and cost of new materials development efforts. In recent research [1,2] the author and co-workers have developed the first unified computational approach to the multiscale (molecular to macro) materials design problem. This paper extends the last cited work, formulating a new model of ab initio molecular dynamics. It differs from previous work in two important respects: (1) the quantum, molecular, and macro (process environment) scales are coupled using a nonholonomic Hamiltonian modeling methodology, and (2) the formulation rigorously satisfies the first and second laws of thermodynamics under conditions of general thermal and mechanical interaction with the external environ-

ment. The development which follows builds upon previous research, conducted by the author and co-workers, formulating and validating models for a variety of complex problems (at various scales and in various reference frames) using a nonholonomic Hamiltonian modeling methodology.

2 NUMERICAL METHOD

The modeled system is a collection of n nuclei and n_e electrons in an NVT ensemble. The Hamiltonian for the system (H) is the sum of the kinetic (T_n) and potential (V_n) energies for the nuclei (which take a molecular dynamics form) and a total energy (E_e) for the electrons (which takes a quantum mechanics form)

$$H = T_n + V_n + E_e \quad (1)$$

The nuclear kinetic co-energy and nuclear momenta are

$$T_n^* = \frac{1}{2} \sum_{i=1}^n M^{(i)} \dot{q}^{(i)2}, \quad p^{(i)} = \frac{\partial T_n^*}{\partial \dot{q}^{(i)}} \quad (2)$$

where $M^{(i)}$ is a nuclear mass and $q^{(i)}$ is a nuclear center of mass position. The nuclear potential energy $V_n(\mathbf{q})$ includes electrostatic repulsion of the nuclei and the effects of any external potential. The quantum mechanics expression for the electronic energy includes electron repulsion, electron-nuclear attraction, and electron kinetic energy, and is computed from the electronic wave function using the expectation value expression (in Dirac bracket notation)

$$E_e = \frac{\langle \Psi | H_e | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad H_e = -\frac{\hbar^2}{m_e} \sum_{j=1}^{n_e} \frac{\partial^2}{\partial x_j^2} + V_e \quad (3)$$

where H_e is the electronic Hamiltonian operator, \hbar is the reduced Planck constant, m_e is an electron mass, V_e is an electronic potential energy, and Ψ is the electronic wave function. Interpolating the wave function with a set of n_s basis functions ϕ_j (in the form of atomic orbitals centered on the nuclei)

$$\Psi = \sum_{j=1}^{n_s} c^{(j)} \phi_j(\mathbf{q}, x) \quad (4)$$

which then defines the discrete stored energy function as $E_e = E_e(\mathbf{q}, \mathbf{c})$ where the $c^{(j)} = c^{(j)}(t)$ are the time dependent weighting coefficients of the basis set. In order to complete the formulation, evolution equations for the time dependent basis coefficients are required. Adopting an Ehrenfest framework, these may be obtained from the Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H_e \Psi \quad (5)$$

Multiplying the Schrodinger equation by the complex conjugate basis function ϕ_k^* and integrating over the modeled volume provides the discrete evolution equations

$$\mathbf{A}\dot{\mathbf{c}} + \mathbf{B}\dot{\mathbf{q}} = \mathbf{H}\mathbf{c} \quad (6)$$

where the matrix coefficients are

$$A_{kj} = i\hbar \int \phi_k^* \phi_j dx, \quad H_{kj} = \int \phi_k^* H_e \phi_j dx \quad (7)$$

and

$$B_{kj} = i\hbar \sum_{l=1}^{n_s} c^{(l)} \int \phi_k^* \frac{\partial \phi_l}{\partial q^{(j)}} dx \quad (8)$$

In the discussion which follows the classical and quantum system dynamics are coupled using a non-holonomic modeling approach.

The canonical Hamilton's equations for the mixed classical-quantum system are

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} + \mathbf{f}^q, \quad \dot{\mathbf{q}} = \mathbf{M}^{-1}\mathbf{p}, \quad \mathbf{0} = -\frac{\partial H}{\partial \mathbf{c}} + \mathbf{f}^c \quad (9)$$

where the inertia matrix \mathbf{M} is diagonal, and \mathbf{f}^q and \mathbf{f}^c are generalized forces due to the nonholonomic constraints. The third Hamilton's equation, a degenerate momentum equation (degenerate since there are no generalized momenta associated with the generalized coordinates \mathbf{c}), has been overlooked in previous ab initio simulation work. However it is of central importance, since it allows the Lagrange multipliers associated with the nonholonomic constraints to be determined in closed form.

The nonholonomic constraints are the Schrodinger equation and a rate relation which quantifies thermal interaction with the environment

$$\theta \dot{S} = R(\theta - \theta_e), \quad \theta = \sum_{i=1}^n \frac{1}{3nk_B} M_i \dot{q}^{(i)2} \quad (10)$$

where \dot{S} is a net entropy flow from the nanoscale ensemble to the environment, θ_e is a controlled environmental temperature (and may vary with time), R is an overall heat transfer coefficient, θ is the ensemble temperature, and k_B is Boltzmann's constant. The effects of external mechanical loading, not included here, may

be accounted for by introducing additional nonholonomic constraints.

Introducing a vector of Lagrange multipliers λ for the discrete Schrodinger equations, the quantum constraints and the thermal dissipation expression require

$$\mathbf{f}^c = \mathbf{A}^T \lambda, \quad \mathbf{f}^q = \mathbf{B}^T \lambda - \frac{R}{3nk_B} \left(1 - \frac{\theta_e}{\theta}\right) \mathbf{p} \quad (11)$$

It follows that the final Hamilton's equations for the NVT ensemble are

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} + \mathbf{B}^T \mathbf{A}^{-T} \frac{\partial H}{\partial \mathbf{c}} - \frac{R}{3nk_B} \left(1 - \frac{\theta_e}{\theta}\right) \mathbf{p} \quad (12)$$

$$\dot{\mathbf{q}} = \mathbf{M}^{-1}\mathbf{p} \quad (13)$$

$$\mathbf{A}\dot{\mathbf{c}} = -\mathbf{B}\mathbf{M}^{-1}\mathbf{p} + \mathbf{H}\mathbf{c} \quad (14)$$

It appears that the formulation just derived is the first to fully exploit nonholonomic Hamiltonian methods in obtaining an energy conserving multiscale multi-physics model of a mixed classical-quantum system.

3 ADVANTAGES OF THE METHOD

Nonholonomic methods offer a canonical Hamiltonian approach to two fundamental modeling issues of wide interest: (1) systematic linking of multiple scales, and (2) systematic linking of multiple energy domains. Alternative approaches which appear in the literature are either limited in scope or introduce new stability or accuracy concerns.

- Born-Oppenheimer methods [3] couple the classical molecular dynamics problem to a static equilibrium model of the electronic structure, neglecting the transient nature of the reacting (quantum chemical) electronic subsystem.
- Car-Parrinello methods [4] introduce a fictitious inertia for the electronic subsystem, in order to obtain a conventional (holonomic) Hamiltonian model of the coupled classical-quantum system. A theoretical basis for this electronic inertia model is lacking, and no general solution to the resulting problem of electronic subsystem oscillations has been found.
- Ehrenfest methods [5] couple the molecular dynamics model to the Schrodinger equations using a constant system energy assumption, certainly not applicable to the materials design problem, where external mechanical and thermal loading play a major role in influencing chemical process dynamics.

In previous work, nonholonomic methods have been applied to model transient chemical processes at both the continuum and nanoscales [6,7]. However applications of nonholonomic methods in nanoscale computational chemistry have to date been very limited. It appears that no previous work has applied nonholonomic methods to address the fundamental issues discussed in this paper: the systematic coupling of scales, the systematic coupling of energy domains, or the development of very general transient formulations.

4 EXAMPLE APPLICATIONS

This section demonstrates two particular advantages of a nonholonomic modeling approach to computational chemistry. Specifically, two extensions of the formulation derived in the last section are described, which introduce the use of: (1) discontinuous cutoff functions, and (2) adaptive basis functions, in order to describe evolution of the electronic structure. The molecule-ion interaction problem described in reference [8] is used to illustrate the modeling concepts of interest. The formulations which follow cannot be obtained from any holonomic modeling approach. It is important to note that the general advantages of the nonholonomic formulation derived in the last section, and the specific examples discussed in this section, apply in general and are not restricted to particular applications.

4.1 Discontinuous Cutoff Functions

The first extension introduces discontinuous cutoff functions to model the electronic structure. The motivation for this extension is well documented in the literature. The plane wave and orbital basis functions typically used in ab initio molecular dynamics modeling extend to infinity, so that in principle the interaction of all nuclei and electrons must be computed at each time step. The high computational cost of full interaction models motivates the introduction of modified basis sets in most practical calculations. In holonomic formulations, discontinuous cutoff functions lead to systematic energy errors; since the modification of basis sets (to eliminate this energy error) also changes interaction forces, holonomic calculations are in general influenced by a fundamental modeling compromise. The nonholonomic modeling approach which follows admits discontinuous cutoff functions and computes exact interaction forces while rigorously satisfying conservation of energy. In the hydrogen molecule-ion problem [8], the discrete electronic Hamiltonian takes the functional form

$$E_e = E_e[\mathbf{c}, q, S_1(q), S_2(q), S_3(q)] = E_e(\mathbf{c}, q) \quad (15)$$

where the S_i ($i = 1, 2, 3$) are Coulomb, resonance, and overlap integrals and q is the single nuclear generalized

coordinate (the nuclei separation distance). If exponential basis functions (paramatized by the Bohr radius constant a_0) are employed, the electronic interpolation functions extend to infinity and the system model takes the form previously described. An alternative approach is to rewrite the electronic Hamiltonian in the form

$$E_e = E_e(\mathbf{c}, S'_1, S'_2, S'_3) \quad (16)$$

where the new generalized coordinates S'_i are defined by the nonholonomic constraints

$$\dot{S}'_i = \frac{\partial S_i}{\partial q} \dot{q} u_s(\alpha a_0 - q), \quad i = 1, 2, 3 \quad (17)$$

with u_s a step function and α the number of Bohr radii at which a discontinuous interaction cutoff is applied. Since the partial derivatives in the last expression involve the original Coulomb, resonance, and overlap integrals, the resulting formulation will produce generalized forces which: (1) match exactly those of an infinite interaction model inside the cutoff region, and (2) are zero outside the cutoff region. The formulation will satisfy exactly conservation of energy, so that the choice of cutoff distance may be made independently, on the basis of accuracy, computational cost, or the characteristics of the physical system of interest. Development of the complete system model proceeds using the techniques previously described, exploiting the degenerate Hamilton's equations

$$0 = -\frac{\partial H}{\partial S'_i} + f^i, \quad i = 1, 2, 3 \quad (18)$$

to determine in closed form the Lagrange multipliers associated with the new constraints. The generalized non conservative forces f^i are determined, as shown previously, from the coefficients in the nonholonomic constraints. The final formulation, for an NVE ensemble, is

$$\mathbf{A}'\dot{\mathbf{c}} = -\mathbf{b}' M^{-1}p + \mathbf{H}'\mathbf{c} \quad (19)$$

$$\dot{p} = -\frac{\partial H}{\partial q} + \mathbf{b}'^T \mathbf{A}'^{-T} \frac{\partial H}{\partial \mathbf{c}} - f \quad (20)$$

$$\dot{q} = M^{-1}p \quad (21)$$

$$\dot{S}'_i = \frac{\partial S_i}{\partial q} M^{-1}p u_s(\alpha a_0 - q) \quad (22)$$

where $i = 1, 2, 3$, and

$$f = \sum_{i=1}^3 \frac{\partial H}{\partial S'_i} \frac{\partial S_i}{\partial q} u_s(\alpha a_0 - q) \quad (23)$$

The primes on the discrete Schrodinger equation coefficients indicate that they are computed using the step-truncated basis functions.

4.2 Adaptive Basis Functions

An interesting feature of the hydrogen molecule-ion problem [8] considered here is that it motivates the consideration of adaptive basis sets, for use in interpolating the electron density. Reference [8] indicates that the principal source of error in the analytical equilibrium solution developed by the cited authors is the inability of the minimum basis set used in their calculations to represent the ‘shrinkage’ of electron orbitals which occurs as the nuclei separation distance is reduced. Hence this section presents a nonholonomic, energy conserving reformulation of the ab initio molecular dynamics model, one which allows for adaptive evolution of basis function parameters. In this case the electronic Hamiltonian takes the functional form

$$E_e = E_e(\mathbf{c}, q, a) \quad (24)$$

where a is a time dependent basis set parameter, replacing the constant Bohr radius (a_0). It’s evolution may be described by a nonholonomic constraint

$$\dot{a} = \chi(\mathbf{c}, q, a) \dot{q} \quad (25)$$

where the choice of a functional form for χ determines the adaptive scaling of the orbital basis set. In the hydrogen molecule-ion problem, the choice may be simply to dynamically scale the interpolating orbitals with the approach velocity for the nuclei, inside a cutoff distance. Note that the function χ need not be continuous or differentiable, for example hard limits may be applied to both the shrinkage and the expansion of the interpolation. Development of the complete system model proceeds using the techniques previously described, exploiting the degenerate Hamilton’s equation

$$0 = -\frac{\partial H}{\partial a} + f^a \quad (26)$$

to determine in closed form the Lagrange multiplier associated with the new constraint. The generalized non-conservative force f^a is determined, as shown previously, from the coefficients in the nonholonomic constraint. The discrete Schrodinger equations will in this case be written

$$\mathbf{A}\dot{\mathbf{c}} + \mathbf{b}\dot{q} + \mathbf{h}\dot{a} = \mathbf{H}\mathbf{c} \quad (27)$$

and the final formulation for an NVE ensemble is

$$\mathbf{A}\dot{\mathbf{c}} = -[\mathbf{b} + \mathbf{h}\chi(\mathbf{c}, q, a)]M^{-1}p + \mathbf{H}\mathbf{c} \quad (28)$$

$$\dot{p} = -\frac{\partial H}{\partial q} + \mathbf{b}^T \mathbf{A}^{-T} \frac{\partial H}{\partial \mathbf{c}} - f \quad (29)$$

$$\dot{q} = M^{-1}p \quad (30)$$

$$\dot{a} = \chi(\mathbf{c}, q, a) M^{-1}p \quad (31)$$

where

$$f = \chi(\mathbf{c}, q, a) \left(\frac{\partial H}{\partial a} - \mathbf{h}^T \mathbf{A}^{-T} \frac{\partial H}{\partial \mathbf{c}} \right) \quad (32)$$

Adaptive interpolations using plane wave basis functions may be developed using a similar approach.

5 CONCLUSION

The nonholonomic modeling approach developed in this paper fundamentally extends current ab initio molecular dynamics methods, which have been developed on the basis of simplifying assumptions that do not apply to the general computational materials design problem.

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