

# The transfer Hamiltonian: a tool for large scale simulations with quantum mechanical forces

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## Abstract

We report a method for the inclusion of accurate quantum mechanical forces in large scale molecular dynamics simulations by defining a transfer Hamiltonian containing only one and two-center terms that are modeled by parametric functions. The parameters of the transfer Hamiltonian are fit such that interatomic forces computed ab initio at the CCSD/DZP level of theory for the reactions  $C_2H_6 \rightarrow 2CH_3$ ,  $Si_2H_6 \rightarrow 2SiH_3$ , and  $Si_2O_7H_6 \rightarrow Si(OH)_3 + SiO(OH)_3$  are accurately modeled. Use of the transfer Hamiltonian, which is electronic state specific, requires several orders of magnitude less time and disk space than do the ab initio calculations, thus they are suitable for treating the quantum region of multi-scale simulations for systems containing  $\approx 10^3$  atoms.

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## 1. Introduction

Molecular dynamics (MD) simulations are a critical tool in understanding the behavior of large molecular systems. Efficient algorithms, combined with high-speed, parallel computing facilities, have made simulations a valuable tool for the assessment of chemo-mechanical behavior of real materials in non-equilibrium environments which may be difficult to study experimentally. In particular, MD permits the study of fracture at the atomistic level, though hybrid atomistic-continuum approaches have found extensive use [1]. In

this technique, simulations are done atomistically near the crack tip, typically using empirically determined classical potentials, and continuum models are used in regions further away from the site of interest, subject to a suitable boundary region, within which the computational methods are coupled.

However, for phenomena that involve breaking bonds or specific quantum states, we require a quantum mechanical (QM) instead of a classical treatment. This is accomplished by embedding a cluster of atoms to be treated quantum mechanically into a many, perhaps  $10^6$  atom, MD simulation. In particular, fracture entails the breaking of bonds and significant charge redistribution, however, in practice, mostly empirical classical potentials are used. For silica, empirically determined

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potentials of van Beest et al. (BKS) and Tsuneyuki et al. (TTAM) consist of pairwise interactions, including Coulombic, repulsive, and dispersive interactions [2,3]. Potentials including three-body terms [4–6], and some which allow charge transfer [7,8] have also been reported for silica and other materials. Although bulk properties of silica have been well characterized with the existing potentials, their ability to redistribute charge and break chemical bonds is not adequate for the critical bond breaking regions. Further, these potentials have to be validated when additional molecular species are introduced into the system. This type of flexibility is needed, as environmental effects such as solvents, or the presence of oxidizing agents, are known to affect the structural performance of real materials and need proper inclusion in the MD [7–10]. As has been said, “...conventional interatomic potential functions used in MD simulations are often fitted to bulk solid properties, and they are not easily transferable to systems containing defects, cracks, surfaces, and interfaces. In these systems, partial charges and other chemical properties of atoms vary dynamically according to the change in the local environment.” They continue, “...environment-dependent charge distribution is crucial for the physical properties of these systems, including fracture toughness” [1]. Quantum mechanics allows charge to properly redistribute (without regard to empirical assumptions of electronegativity), is readily adaptable to systems of varying complexity, and has the fundamental capability to correctly describe bond dissociation.

## 2. Parameterization of the transfer Hamiltonian

High level *ab initio* methods such as coupled cluster theory can produce results which rival experiment, hence they are predictive. Further, they are applicable to ground, excited, and transition states, though the computational cost usually limits such methods to molecules with a small number of atoms so they are not useful for large scale MD. Density functional methods sacrifice the computational rigor of wavefunction methods leading to greater applicability. Though larger scale applications can be made with density func-

tional methods, when closely tied to MD, the methods are still limited to a few hundred atoms.

Semi-empirical (SE) quantum chemical methods, which are applicable to  $10^3$  atoms, are sufficient for “on the fly” MD, especially when used in conjunction with linear scaling techniques [11]. However, the traditional SE methods previously used in small scale simulations suffer from known deficiencies which can adversely affect an MD simulation [12]. A practical alternative which retains the speed of SE methods, yet introduces information obtained at the *ab initio* level, is reparameterization of SE Hamiltonians against correlated *ab initio* calculations. This has been suggested previously by Truhlar as an interpolation technique for *ab initio* potential energy surfaces [13]. Here we extend the concept by introducing a transfer Hamiltonian built upon the similarity transformed Hamiltonian of coupled cluster (CC) theory whose eigenfunction is a single Slater determinant, yet its eigenvalues and associated forces are exact for all states.

In CC theory, the ground state wavefunction is given by

$$|\Psi_g\rangle = \exp(T)|\phi_0\rangle \quad (1)$$

where  $|\phi_0\rangle$  is a single Slater determinant typically chosen to be the SCF solution and  $T$  is determined from solution of the CC equations (for a comprehensive review of coupled cluster theory and its application to chemistry, see [14]). Insertion of Eq. 1 into the Schrodinger equation gives

$$\exp(-T)H \exp(T)|\phi_0\rangle = E|\phi_0\rangle \quad (2)$$

$$\bar{H}|\phi_0\rangle = E|\phi_0\rangle \quad (3)$$

which is an eigenvalue problem involving an effective Hamiltonian  $\bar{H} = \exp(-T)H \exp(T)$ .  $\bar{H}$  is related to the usual Hamiltonian via a similarity transformation, and as such, it has the same spectrum of eigenvalues as the bare Hamiltonian, however, the ground state eigenfunction of  $\bar{H}$  is the single Slater determinant  $|\phi_0\rangle$  which satisfies Hartree–Fock like equations though all correlation is included. The eigenvalue  $E$  in Eq. 3, and associated forces  $\partial E/\partial R$ , are exact.

$\bar{H}$  may be written in second quantized form as

$$\begin{aligned} \bar{H} = & \sum_{p,q} \bar{f}_{pq} p^+ q + \frac{1}{2!} \sum_{p,q,r,s} \overline{\langle pq || rs \rangle} p^+ q^+ sr \\ & + \frac{1}{3!} \sum_{p,q,r,s,t,u} \overline{\langle pqr || stu \rangle} p^+ q^+ r^+ uts + \dots \end{aligned} \quad (4)$$

whose matrix elements are given in terms of many-body integrals and T amplitudes taken from the reference state coupled cluster calculation [15]. Using the properties of the single determinant reference state, and assuming renormalization of the lower order terms to include effects of the three and higher body interactions, we can extract the one and two partial parts of  $\bar{H}$  to obtain a generalized, correlated, Fock-like operator in the atomic orbital basis called a transfer Hamiltonian ( $T_h$ ),

$$T_h = \sum_{\mu,\nu} [\tilde{h}_{\mu\nu} + \sum_{\lambda,\sigma} P_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle] \tilde{\mu}^+ \tilde{\nu} \quad (5)$$

$P_{\lambda\sigma}$  is an element of the density matrix  $P = CnC^+$  where  $C$  is a matrix of eigenvectors and  $n$  is a diagonal matrix of occupation numbers.

In Eq. (5), the matrix elements  $\tilde{h}_{\mu\nu}$  and  $\langle \mu\lambda || \nu\sigma \rangle$  are calculated from purely atomic parameters whose functional forms may be chosen freely. In this work, we have adopted the neglect of diatomic differential overlap (NDDO) form from SE quantum chemistry [16] however, the formalism is not limited to this choice. Specifically, we employ the AM1 implementation [17] and the corresponding functional forms for the one and two-electron integrals [19] and the core–core repulsion terms. Within the NDDO approximation, the charge distributions are restricted to basis functions on the same center. This gives, at most, two-atom interactions whereas  $T_h$  formally has no such restriction. Here, we have assumed this generalized two-atom Fock-like operator form, though some consideration of how to incorporate the higher order terms present in  $\bar{H}$  into a suitable NDDO scheme has been made in a related approach due to Freed [20].

To obtain  $T_h$ , a non-linear optimization algorithm is used to define the atomic parameters in the NDDO Hamiltonian [13]. In this scheme, a set of reference data (i.e. energies, forces, force constants, etc.) is generated via a high level, ab initio

computation and the NDDO Hamiltonian is reparameterized such that it provides the reference data at the chosen points. The usual approach is minimization of a “cost function” defined to be the sum of the squares of the differences between the calculated and reference values. This cost function, which depends parametrically on the NDDO parameters, is then minimized using a genetic algorithm to locate the global minimum. The parameters which result from the genetic algorithm are further refined using a quasi-Newton optimization algorithm to ensure that the parameters are stationary.

Since accurate cartesian forces are required to perform MD simulations, we have chosen to minimize the error function

$$f = \sum_{i=1}^{\text{NPTS}} [ \|F_i^{\text{NDDO}}\| - \|F_i^{\text{CCSD}}\| ]^2 \quad (6)$$

where the reference quantities  $\|F_i^{\text{CCSD}}\|$  are the cartesian gradient norms resulting from a CCSD calculation, at the  $i$ 'th point, along a distinguished coordinate path (DCP). Typically, NPTS is chosen to be in the range 8–11 depending on the size of the molecule. It should be noted that the cost function is not limited to the form presented in Eq. (6). One may also construct cost functions which contain weighted sums of errors for various types of reference data, i.e. gradient norms and force constants; cost functions of this type have been used in some of our work as well.

Given a set of parameters which defines  $T_h$ , we solve

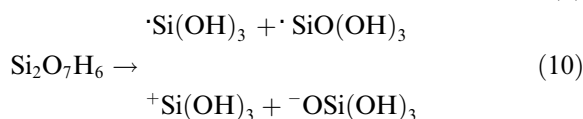
$$T_h C = S C \epsilon \quad (7)$$

where  $S$  is the atomic overlap matrix and  $C$  is a matrix of molecular orbital coefficients. In general, the overlap is included in our scheme, though the choice of the NDDO functional form made in this work sets the overlap matrix equal to the unit matrix. The transfer Hamiltonian is solved self consistently, properly includes the overlap (when necessary), and is of two-atom type instead of invoking a nearest neighbor assumption like tight binding calculations. Furthermore it provides an energy and forces which are formally exact. Self consistency is critical for the proper description of

bond breaking and also permits the study of different electronic states.

### 3. Results

As our primary objective is to describe bond breaking in materials, systems such as silica and hydrocarbons are of special interest. Parameter sets for the following dissociation reactions of ethane, disilane, and pyrosilic acid (see Fig. 1),



have been determined using the PIKAIA [21] and L-BFGS-B [22] codes which are genetic and quasi-Newton algorithms, respectively. The ab initio reference data (forces as a function of geometry) was generated at the CCSD/DZP level of theory, and we have chosen the AM1 variant of NDDO Hamiltonian as the functional form for the transfer Hamiltonian. This choice was predicated upon work done by Hsiao et al. [12] who did an MD study of C60 impacting upon a passive surface using a variety of NDDO Hamiltonians. In that work, AM1-NDDO was superior to other functional forms.

We consider the atomic parameters characteristic of the AM1-NDDO Hamiltonian to fall into three categories:

- Those due to the core–core repulsion [16].
- Electronic parameters for s and p atomic orbitals [17].

- Electronic parameters for d atomic orbitals [18].

When the first is sufficient, as it is for pyrosilic acid, only the core–core repulsion parameters are optimized and the remaining parameters are held fixed at the standard AM1 values.

Figs. 2–5 show comparisons of the forces along the distinguished coordinate (C–C, Si–Si, and bridged Si–O bond for reactions (8)–(10), respectively). In the first two curves, all geometric degrees of freedom are relaxed as the distinguished coordinate is broken, however, in the case of pyrosilic acid, as a model for bulk, amorphous silica, the Si–O–H units are constrained to be 120° and the O–H bond length is fixed at its equilibrium value.

The force profile resulting from the standard AM1-NDDO parameter set, at intermediate/long ranges, is seen to be in gross error in comparison to the ab initio reference points, however, this is largely rectified with the transfer Hamiltonian (TH-CCSD). Furthermore, insisting upon the two-atom form of the NDDO Hamiltonian, we expect the purely atomic parameters to saturate with nominal cluster size. Once this is accomplished, it is expected that the transfer Hamiltonian will provide an improved description of the quantum region of an MD simulation for systems similar to those used in the parameterization (i.e. extended Si–O systems).

It should also be noted that the transfer Hamiltonian description of the two dissociation paths to charged and neutral fragments given in Eq. (10), can be well modeled with the same parameter set. These two dissociation pathways are modeled by

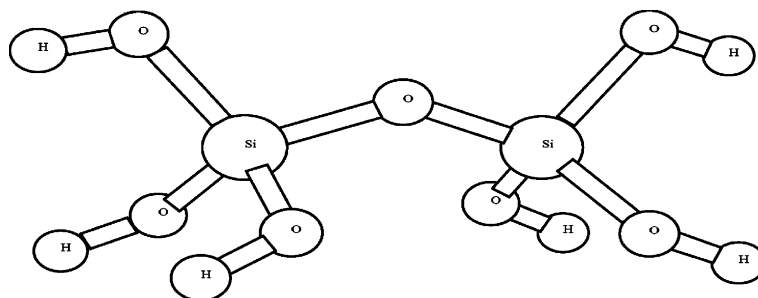


Fig. 1. Structure of pyrosilic acid.

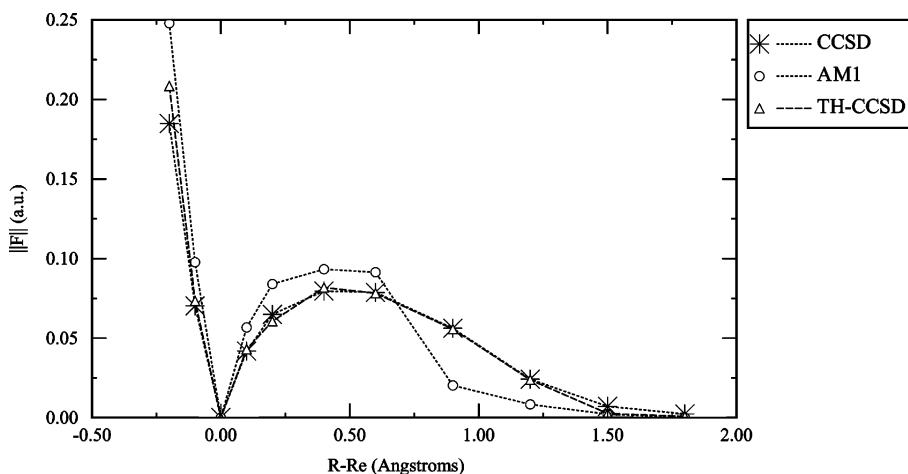


Fig. 2. Comparison of forces from standard semi-empirical theory (AM1) and the Transfer Hamiltonian (TH-CCSD) with coupled cluster (CCSD) results for dissociation of ethane.

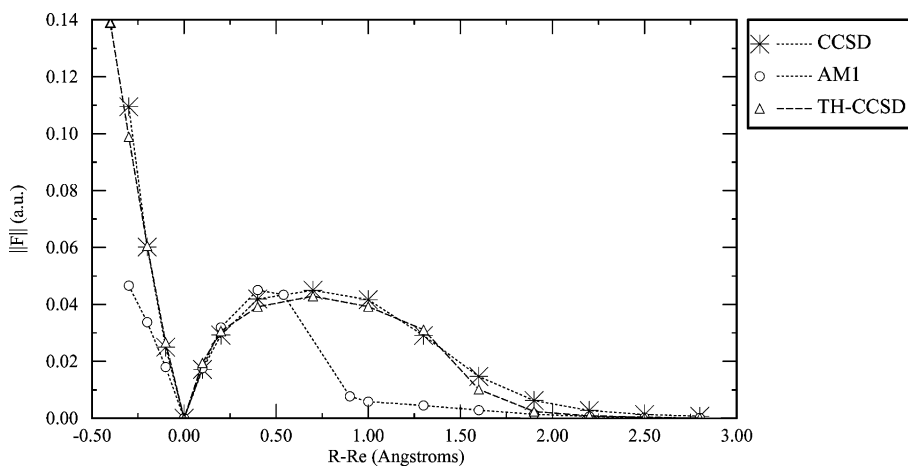


Fig. 3. Comparison of forces from standard semi-empirical theory (AM1) and the Transfer Hamiltonian (TH-CCSD) with coupled cluster (CCSD) results for dissociation of disilane.

employing restricted (separation into charged fragments) and unrestricted (separation into neutral fragments) Hartree–Fock calculations using the same parameter set. Although the ab initio reference data pertaining to the dissociation into neutral fragments (the lower energy pathway by  $\approx 30$  kcal/mol) was the only data included in the parameterization, the force curve (Fig. 5) resulting from dissociation into charged fragments, which was not explicitly included in the fitting scheme, is also well described. This introduces the concept of

electronic state specificity in MD simulations. Since the transfer Hamiltonian is solved self consistently, forces corresponding to different dissociation pathways may be used to drive the MD simulation. This type of flexibility is important for the study of fracture since a variety of dissociation paths will certainly occur. Furthermore, for a description of optical properties, we require electronic state specificity.

Generation of the force profiles given in Figs. 2 through 5 require calculations of the total energy

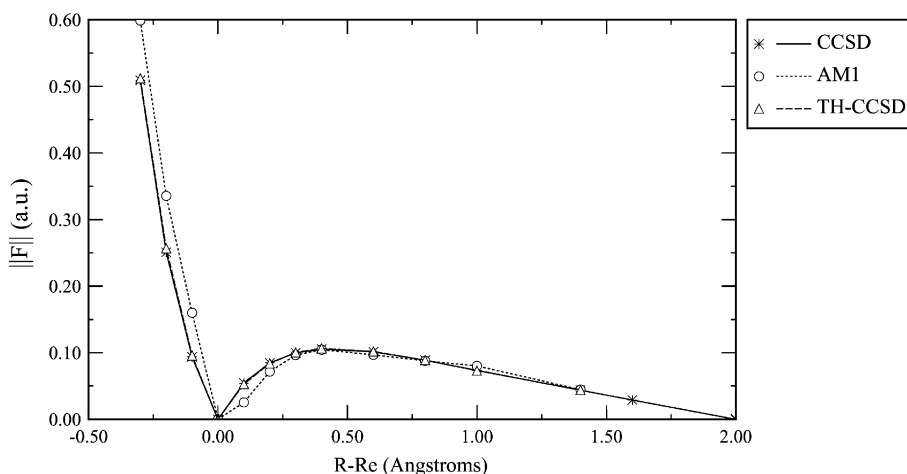


Fig. 4. Comparison of forces from standard semi-empirical theory (AM1) and the Transfer Hamiltonian (TH-CCSD) with coupled cluster (CCSD) results for dissociation of pyrosilicic acid into neutral fragments.

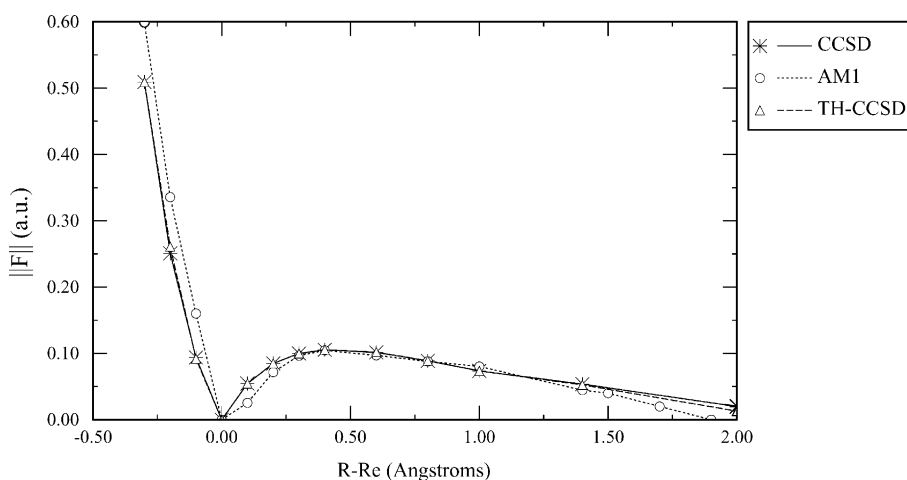


Fig. 5. Comparison of forces from standard semi-empirical theory (AM1) and the Transfer Hamiltonian (TH-CCSD) with coupled cluster (CCSD) results for dissociation of pyrosilicic acid into charged fragments.

and differentiation of the energy with respect to the 3 N cartesian coordinates. Table 1 compares the CPU time for an energy and gradient calculation at the transfer Hamiltonian and ab initio CCSD levels. Although the transfer Hamiltonian well reproduces results from the ab initio computations, it performs orders of magnitude more quickly and is fast enough to be used in large scale MD simulations. This is the advantage of the transfer Hamiltonian.

Fig. 6 shows comparisons of the shape of the PES along the distinguished coordinate for the two dissociation paths of pyrosilicic acid given in Eq. (10). The plotted CCSD energies result from standard single point energy calculations along the DCP where the equilibrium minimum energy value was used as a reference. On the contrary, the AM1-NDDO and transfer Hamiltonian PES' were determined via integration of the forces (which yields energy differences) at various points along

Table 1

Computer time (CPU seconds) required to perform one energy/gradient calculation for the systems studied

Molecule	CCSD	DFT	TH-CCSD
C <sub>2</sub> H <sub>6</sub>	45.1	41.1	0.02
Si <sub>2</sub> H <sub>6</sub>	104.8	55.6	0.02
Si <sub>2</sub> O <sub>7</sub> H <sub>6</sub>	8656.1	685.1	0.08

The ab initio calculations and transfer Hamiltonian (TH-CCSD) calculations were performed using ACESII [23] and MNDO97 [24], respectively. All calculations were run on an IBM RS/6000.

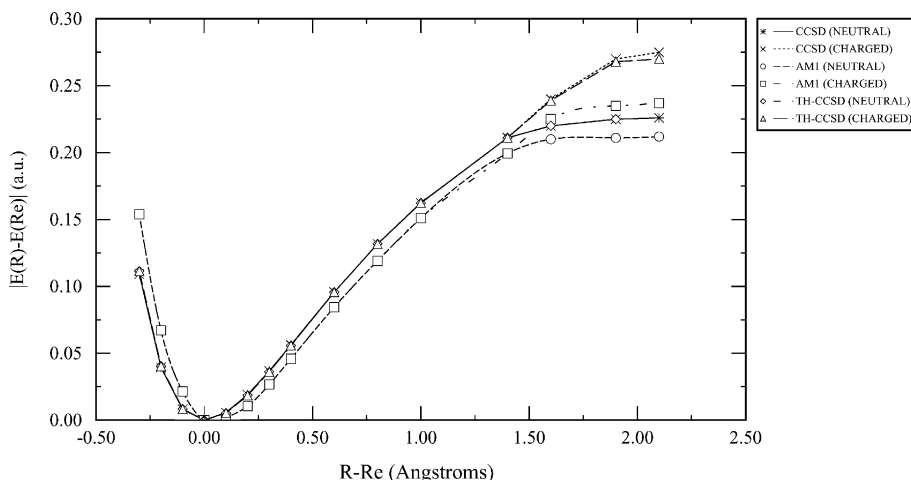


Fig. 6. Comparison of PES for dissociation of pyrosilicic acid. Each curve is labeled by the Hamiltonian used and the dissociation path followed.

the DCP. The PES resulting from the standard AM1-NDDO parameterization is seen to underestimate the dissociation energy for each path. The use of the transfer Hamiltonian gives PES' for each dissociation path which are quantitatively correct although no "explicit" inclusion of energy differences was included in the parameterization scheme as the reference data was forces as a function of geometry.

#### 4. Summary

We have introduced the concept of a transfer Hamiltonian as a low rank operator that permits the rapid calculation of QM forces to drive MD simulations. Guided by the NDDO form of Hamiltonian used in semi-empirical quantum

chemistry, we have determined transfer Hamiltonians for several prototype molecules. The new parameters largely correct the errors given by the conventional AM1 variant of the NDDO Hamiltonian, and, provided that the atomic parameters which define the transfer Hamiltonian are saturated by small clusters, can be applied to large scale MD simulations of systems similar to the calibration clusters. Furthermore, as illustrated for pyrosilicic acid, different electronic states corresponding to different dissociation paths are equally well described with the same set of atomic parameters. This introduces the concept of electronic state specificity in MD simulations due to the ability of the transfer Hamiltonian to describe radicals, cations, and anions, which, with most classical potentials, is not possible.

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