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ACHIEVING PREDICTIVE SIMULATIONS WITH QUANTUM MECHANICAL FORCES VIA THE TRANSFER HAMILTONIAN: PROBLEMS AND PROSPECTS

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1. Prologue

According to the Westmoreland report [1], “in the next ten years, molecularly based modeling will profoundly affect how new chemistry, biology, and materials physics are understood, communicated, and transformed to technology, both intellectually and in commercial applications. It creates new ways of thinking – and of achieving.”

Computer modeling of materials can potentially have an enormous impact in designing or identifying new materials, how they fracture or decompose, what their optical properties are, and how these and other properties can be modified. However, materials’ simulations can be no better than the forces provided by the potentials of interaction among the atoms involved in the material. Today, these are almost invariably classical, analytical, two- or three-body potentials, because only such potentials permit the very rapid generation of forces required by large-scale molecular dynamics. Furthermore, while such potentials have been laboriously developed over many years, adding new species frequently demands another long-term effort to generate potentials for the new interactions. Most simulations also depend upon idealized crystalline (periodic) symmetry, making it more difficult to describe the often more technologically important amorphous materials. If we also want to observe bond breaking and formation, optical properties, and chemical reactions, we must have a quantum mechanical basis for our simulations. This requires a multi-scale philosophy, where a quantum mechanical core is tied to a classical

S. Yip (ed.),
Handbook of Materials Modeling, 27–57.

atomistic region, which in turn is embedded in a continuum of some sort, like a reaction field or a finite-element region.

It is now well-known that *ab initio* quantum chemistry has achieved the quality of being "predictive" to within established small error bars for most properties of isolated, relatively small molecules, making it far easier to obtain requisite information about molecules from applications of theory, than to attempt complicated and expensive experimental observation. In fact, applied quantum chemistry as implemented in many widely used computer programs, ACES II [2], GAUSSIAN, MOLPRO, MOLCAS, QCHEM, etc, has now attained the status of a tool that is complimentary to those of X-ray structure determination and NMR and IR spectra in the routine determination of the structure and spectra of molecules. However, there is an even greater need for the computer simulations of complex materials to be equally predictive. Unlike molecules, which can usually be characterized in detail by spectral and other means, materials are far more complex and cannot usually be investigated experimentally under similarly controlled conditions. They have to be studied at elevated temperatures and under non-equilibrium conditions. Frequently, the application of the material might be meant for extreme situations that might not even be accessible in a laboratory. Hence, if we use more economical computer models to learn how to suitably modify a material to achieve an objective, our materials simulations must be "predictive," to trust both the qualitative and quantitative consequences of the simulations.

Besides the predictive aspect, another theme that permeates our work with materials is "chemistry." By chemistry we mean that unlike the idealized systems that have been the focus of most of the simulation work in materials science, we want to consider the essential interactions among many different molecular species; and, in particular, under stress. As an example, a long unsolved problem in materials is why water will cause forms of silica to weaken by several orders of magnitude compared to their dry forms [3–5] while ammonia with silica shows a different behavior. A proper, quantum mechanically based simulation should reflect these differences, qualitatively and quantitatively.

The third theme of our work is that by virtue of using a quantum mechanical (QM) core in multi-scale simulations, unlike all the simulations based upon classical potentials, we have quantum state specificity. In a problem like etching silica with CF_4, which generates the ething agent, CF_3, a classical potential cannot distinguish between CF_3^+, CF_3^-, and $CF_3^{\cdot}$, yet obviously the chemistry will be very different. Furthermore, we also have need for the capability to use excited electronic states in our simulations, to include species like CF_3^*, e.g., or to distinguish between different modes of fractures of the silica target, such as radical dissociation as opposed to ionic dissociation.

Conventionally, the only quantum mechanically based multi-scale dynamics simulations that would permit as many as 500–1000 atoms in the QM region were based upon the tight-binding (TB) method, density functional theory

(DFT) being used only for smaller QM regions. TB is a pervasive term that covers everything from crude, non-self-consistent descriptions like extended Hückel theory [6], to quasi-self-consistent schemes based upon Mulliken or other point charges [7], to a long history of solid state efforts [8, 9], to TB with three-body terms [10]. The poorest of these do not introduce overlap, self-consistency, nor explicit consideration of the nuclear–nuclear repulsion terms that would be essential in any ab initio approach; so in general such methods cannot correctly describe bond breaking, where charge transfer is absolutely essential. However, there have been significant improvements on several fronts in the recent TB literature [11, 12] which are helping to rectify these failings.

The alternative approach to TB is that based upon the semi-empirical quantum chemistry tradition starting with Pariser and Parr [13, 14], Dewar *et al.* [15, 16] and Pople *et al.* [17, 18], and being extended on several fronts by Stewart [19–21], Thiel [22], Merz [23], Repasky *et al.* [24], and Tubert-Brohman *et al.* [25]. These "neglect of differential overlap methods," of which the most flexible is the NDDO method, meaning "neglect of diatomic differential overlap" will be our initial focus. Like TB methods, the Hamiltonian is greatly simplified but not necessarily by limiting all interactions to nearest neighbors, but instead to operationally limiting interactions to mostly diatomic units in molecules. We will address some of the details later, but for most of our purposes, the particular form for the "*transfer Hamiltonian*" will be at our disposal and suitable forms with rigorous justification are a prime objective of our research.

It might be asked why a "Hamiltonian" instead of a potential energy surface? Fitting the latter especially while including the plethora of bond-breaking regions, is virtually impossible for even simple molecules. Highly parameterized molecular mechanics (MM) methods [26] can do a good job of generating a potential energy surface near equilibrium for well-defined and unmodified molecular units; but bond breaking and formation is outside the scope of MM. So our objective, instead of the PES (potential energy surface), is to create a "transfer Hamiltonian" that permit the very rapid determination of, in principle, all the properties of a molecule; and especially the forces on a PES for steps of the MD. The transfer Hamiltonian gives us a way to subsum *most of the complications of a PES in a very convenient package that will yield the energy and first and second derivatives upon command.* This has been done to some degree in rate constant applications for several atom molecules where the complication is the need for multi-dimensional PES information [27–29]. Here, we conceive of the transfer Hamiltonian as a way to get *all* the relevant properties of a molecule including its electronic density, and related properties like dipole moments, and its photoelectron, electronic, and vibrational spectra. Except for the latter, these are purely "electronic" properties, which depend solely on the electronic Schrödinger equation. These should be distinguished from forces and the PES itself, which are properties of the total energy.

The distinction between the two has been at the heart of the principal dilemma in simplified or semi-emprirical theory, where a set of parameters that give the total energy are not able to describe electronic properties equally well. It is also critical that the Hamiltonian be computed very rapidly to accomodate MD applications, and a form for it needs to be determined such that we retain the accuracy of the forces and other properties that would come from *ab initio correlated theory.* This is more an objective than a *fait-accompli*, but we will discuss how to try to accomplish this in this contribution.

Our approach is to appeal to the highest level of *ab initio* quantum chemistry, namely coupled-cluster (CC) theory, to use as a basis for a "transfer Hamiltonian" that embed the accurate, predictive quality CC forces taken from suitable clusters into it, but in an operator that is of very low rank, making it possible to do fully self-consistent calculations on $\sim$500–1000 atoms undergoing MD. Hence, as long as a phenomena is accessible to MD, and if the transfer Hamiltonian forces retain the accuracy of CC theory, we should be able to retain the predictive quality of the CC method in materials simulations; and if we can also describe the electronic properties accurately, we have everything that the Schrödinger equation could tell us about our system. In addition, we have no problem with changing atoms or adding new molecules to our simulations, as our transfer Hamiltonian is applicable to any system once trained to ensure its proper description. We will also develop the transfer Hamiltonian approach from DFT considerations in the following to show the essential consistency between the wavefunction and density functional methods.

Our emphasis on predictability, chemistry, and state specificity, offers a novel perspective in the field; and the tools we are developing, all tied together with highly flexible software, sets the stage for the kinds of simulations that will lead to reliable materials design. As the Westmoreland report further states, 'The top needs required by industry are methods that are "bigger, better, faster;" (with) more extensive validation, and multiscale techniques.'

2. Introduction

Our objective is predictive simulations of materials. The critical element in any such simulation are the forces that drive the molecular dynamics. For a reliable description of bond breaking, as in fracture or chemical reaction, or to distinguish between a free radical and a cation or anion, to be electronic state specific; or to account for optical spectra; the forces must be obtained from a quantum mechanical method. Today's entirely first-principles, quantum chemical methods are "predictive" for small molecules in the sense that with a suitable level of electron correlation, notably with coupled-cluster (CC) theory [30], and large enough basis sets [30, 31]; or to a lesser extent, density functional theory (DFT) [32–34] the results for molecular structure, spectra, energetics and the associated atomic forces required for these quantities and for reaction paths are competitive with experiment. In particular, these highly correlated methods offer accurate results for transient molecules and other experimentally inaccessible species, and particularly reaction paths that can seldom be known from solely experimental considerations. In terms of *ab initio* theory, the established paradigm of results from converging, correlated methods is MP2 < CCSD < CCSD(T) < CCSDT < CCSDT(Q_f) < CCSDTQ < Full CI. The acronyms mean, second-order many-body perturbation theory (MBPT(2), subject to a Hartree–Fock reference (Moeller–Plesset), coupled-cluster single and double excitations, plus a non-iterative triples contribution, (T), plus full CC triples, a non-iterative factorized quadruple contribution, and full quadruples; while the ultimate result in a basis set is the full configuration interaction result. Though the latter can only be obtained for some small molecules in small basis sets, it provides an unambiguous reference point for the "right" answer in the basis set (Fig. 1). Notice the comparative convergence of configuration interaction (CI) methods as a function of excitation level, order-by-order MBPT, and CC theory. The basis set, itself, means the atomic orbital basis composed of combinations of gaussian orbitals (contracted), which have been determined from various criteria to span configuration space in a systematic fashion. The results in Fig. 1 use a double-zeta plus polarized basis set, consisting of 4s functions, two sets of p functions and a set of d functions per atom. We have increasingly accurate bases, cc-pVXC [35] where X ranges from 2 to 6. When $X = 2$, we only have s and p orbtials on H, with s, p, d orbitals on heavier atoms in the first row, C, N, O, F, etc. When we go to a second row atom like Si, we pick up another s, p set and a set of d functions as

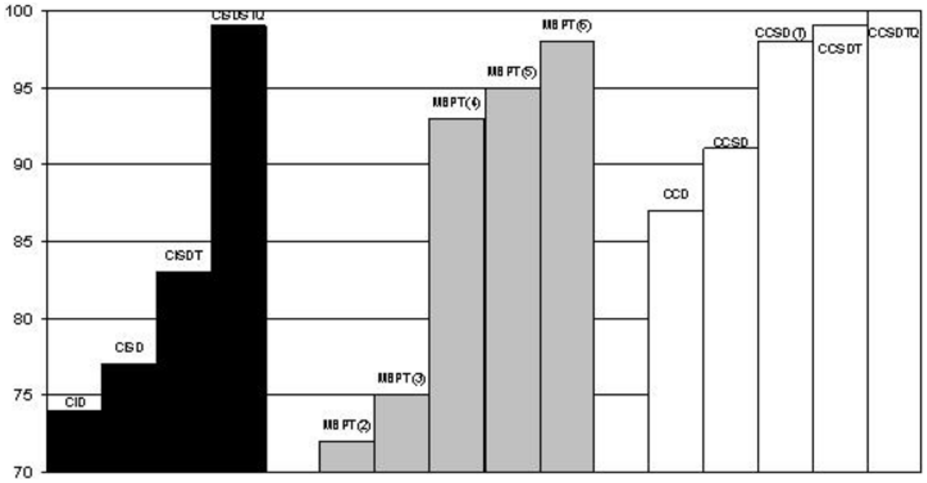

Figure 1. Comparison of CI, MBPT, and CC results with full CI. Results Based on DZP basis for BH, and H_2O at Re, 1.5Re, and 2.0Re.

well. When we go to $X = 3$, we get a third s, third set of p functions, a second set of d functions, and a set of f functions. Clearly, we rapidly go to quite large basis sets when $X \geqq 3$. The fundamental problem with using these methods for large molecules is that after MP2 ($\sim n^5$) the above CC calculations scale non-linearly with the number of basis functions, as $\sim n^6$ for CCSD, $\sim n^7$ for (T), $\sim n^8$ for CCSDT, etc.

The CC methods now in wide use were developed by the Bartlett group from 1978 to the present [36], and have now been implemented numerous times by independent researchers. As for benchmarks toward experiment, many studies of expected error bars exist in the literature for various levels of CC. Notably, the book by Helgaker *et al.* [31] shows many comparisons. We plot the normal distributions of their results for HF, CCSD and CCSD(T) in Figs. 2–4 for the pVDZ and pVTZ bases**.** All *ab initio* results depend upon the quality of the basis set as well as the correlation corrections. We can summarize the results in Table 1.

With a triply polarized basis like cc-pVTZ, the CCSD(T) standard deviations are for structure (~0.0023 Å), dissociation energies for single bonds (~3.5 kcal/mol), harmonic vibrational frequencies(~5–20 cm^{-1}), excitation energies (~0.1 eV for singly excited states) and NMR coupling constants (~5 Hz), with similar ones for other properties. From the normal distributions of errors for bond lengths, dissociation energies, and heats of atomization in small molecules at various levels of theory, there is a dramatic improvement of CC methods over SCF, CISD, MP2. There can also be a significant difference between CCSD and CCSD(T) where the triple excitations are added in a non-iterative form to CCSD [36]. There is an inadequate database about transition states and activation barriers, since few are known experimentally.

For complex systems of the type addressed by modern multi-scale simulations [39, 40], maintaining a chain of approximations built upon the quantum mechanical core like the paradigm above to retain the predictability of the underlying forces is even more important, as there is seldom the extent and quality

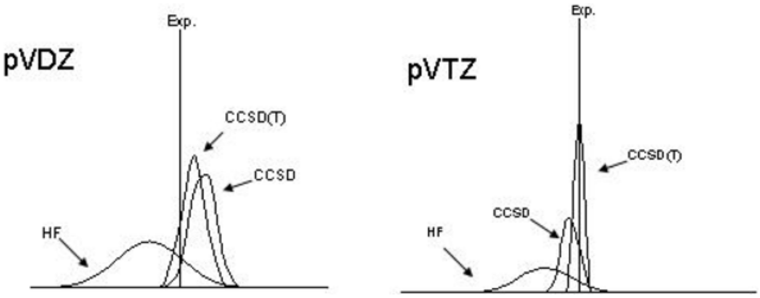

Figure 2. Normal distributions of the errors in calculated bond distances for a set of 28 molecules containing first row atoms.

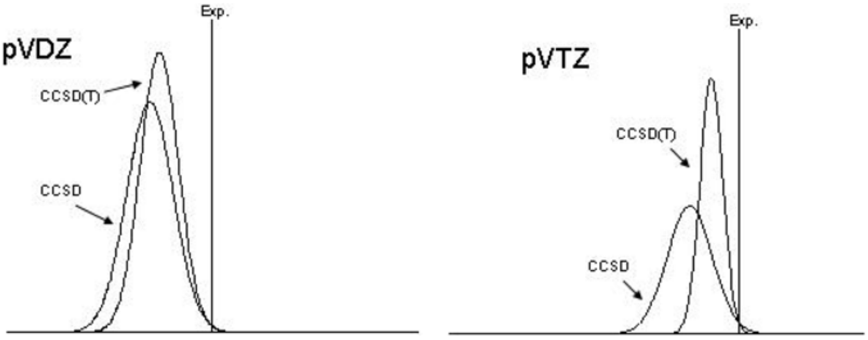

Figure 3. Normal distributions of the errors in calculated atomization energies for a set of 16 molecules containing first row atoms.

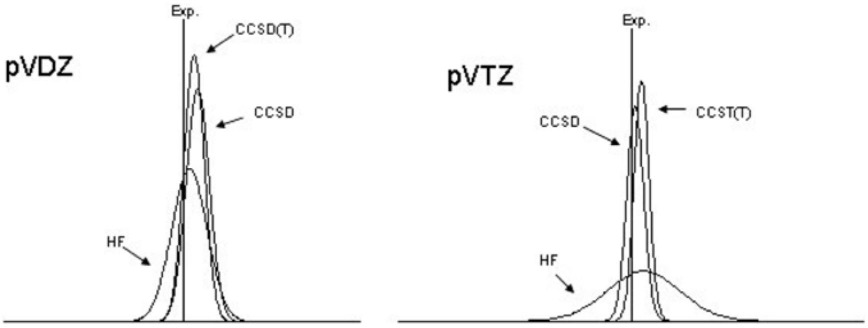

Figure 4. Normal distributions for the errors in calculated reaction enthalpies for a set of 13 reactions containing first row atoms.

Table 1. Bond lengths and dissociation energies as a function of basis set and method [37, 38]

	Band length		Dissociation energy	
	DZ	TZ	DZ	TZ
HF	0.021	0.028	7.12	6.85
MP2	0.013	0.006	7.41	3.28
CCSD(T)	0.016	0.002	8.78	2.88

of molecular specific experimental data available to test the theory that there is for small molecules Hence, evolving toward predictive simulations is critical to obtaining accurate, qualitative and quantitative conclusions. So how can we achieve the predictability we need for materials simulations? The problem is illustrated in Fig. 5. We can do highly accurate studies of molecular structure, spectra, and bond breaking for ∼20 atoms at the CC level; ∼50–200 at the MP2 level; and ∼100–300 at the DFT level. In an isolated case for the energy at a

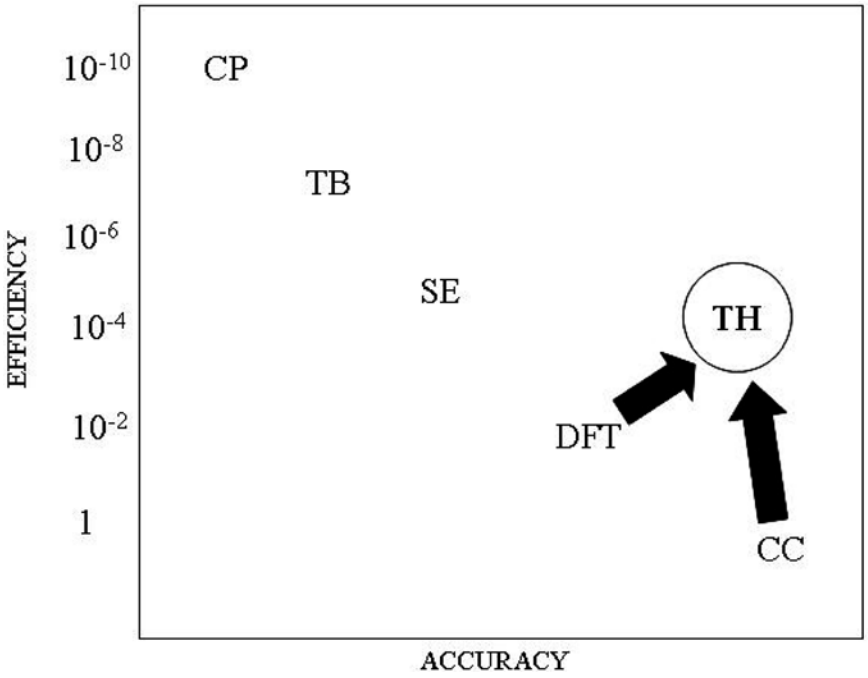

Figure 5. Computational accuracy and efficiency of available potential forms compared to the transfer Hamiltonian.

single geometry (not necessarily forces) with additional tricks we can go much further to ∼1000 atoms [41, 42]. But here we are only concerned with methods for the forces that can be done on a time scale that can be reasonably tied to MD. This imposes a severe limitation on the size of system that can be addressed.

The "transfer Hamiltonian" concept [43, 44] is meant to be a way to retain much of the accuracy of *ab initio* quantum chemistry, like that from CCSD; but in a way that permits the description of ∼500–1000 atoms to be described by QM forces within a time-frame that can be tied to dynamics. We will first consider the wavefunction viewpoint and then that from DFT. After discussing the formal structure, we will specify to a particular form for the transfer Hamiltonian and illustrate its application with numerical results.

3. Transfer Hamiltonian: Wavefunction Approach

In the correlated CC theory we start with the time-independent Schrödinger equation,

$$H\Psi = E\Psi \tag{1}$$

$$\Psi = \exp(T)|0\rangle \tag{2}$$

and introduce the CC ansatz, by writing the wavefunction in the exponential form of Eq. (2). The operator

$$
\begin{aligned}
T &= T_1 + T_2 + T_3 + \cdots && (3)\\
T_1 &= \sum_{a,i} t_i^a \{a^\dagger i\} && (4)\\
T_2 &= \sum_{i>j.a>b} t_{ij}^{ab} \{a^\dagger i b^\dagger j\} && (5)\\
T_3 &= \sum_{i>j>k,a>b.c} t_{ijk}^{abs} \{a^\dagger i b^\dagger j c^\dagger k\} && (6)
\end{aligned}
$$

The T_1 generates all single excitations, i.e., $T_1|0\rangle{=}\sum_{a,i} t_i^a \Phi_i^a$ from the vacuum, usually HF (but could equally well be the Kohn–Sham determinant), meaning excitation of an electron from an occupied orbital to an unoccupied one. We use the convention that i, j, k, l represent orbitals occupied in the Fermi vacuum, while a, b, c, d are unoccupied, and p, q, r, s are unspecified. T_2 does the same for the double excitations, and T_3 the triple excitations. Continuation through T_n for n electrons will give the full CI solution. Multiplying the Schrödinger equations from the left by $\exp(-T)$, the critical quantity in CC theory is the similarity transformed Hamiltonian,

$$\exp(-T)H\exp(T) = \overline{H} \tag{7}$$

where the Schrodinger equation becomes,

$$\overline{H}|0\rangle = E|0\rangle \tag{8}$$

$|0\rangle$ is the Fermi vacuum, or an independent particle wavefunction, but $E(\mathbf{R}) = \langle 0|\overline{H}|0\rangle$ is the exact energy at a given geometry, and the exact forces subject to atomic displacement are

$$\nabla E(\mathbf{R}) = \mathbf{F}(\mathbf{R}) \tag{9}$$

The effects of electron correlation are contained in the cluster amplitudes, whose equations at a given $\mathbf{R}$ are

$$Q_n\overline{H}|0\rangle = 0$$

where $\mathrm{Q}_1 = |\Phi_i^a\rangle\langle\Phi_i^a|$, $Q_2 = |\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}|$, $Q_3 = |\Phi_{ijk}^{abc}\rangle\langle\Phi_{ijk}^{abc}| + \cdots$. Q_1 projections give the equations for $\{\mathrm{t}_i^a\}$, and similarly for the other amplitudes. Limiting ourselves to single and double excitations, we have CCSD which is a highly correlated, accurate wavefunction. Consideration of triples provides, CCSDT, the state-of-the-art; while for practical application, its non-iterative forms CCSD[T] and its improved modification, CCSD[T]; is currently considered the “gold standard” for most molecular studies [36, 43].

Regardless of choice of excitation, $\overline{H}$ may be written in second-quantization as

$$\overline{H} = \overline{h}^{p}_{q}\,\hat{p}^{\dagger}\hat{q} + \frac{1}{2}\overline{g}^{pq}_{rs}\,\hat{p}^{\dagger}\hat{q}^{\dagger}\hat{s}\,\hat{r} + \mathrm{III} + \mathrm{IV} + \cdots \tag{10}$$

where summation of repeated indices is assumed and III and IV indicate three- and four-body operators. The indices can indicate either atomic or molecular orbitals. More explicitly, $\overline{g}^{pq}_{rs} = \overline{\langle pq|rs\rangle} = \overline{(pr|qs)} = \int d1 \int d2\phi^{*}_{p}(1)\phi_{r}(1)g_{12}\phi^{*}_{q}(2)\phi_{s}(2)$ where the latter two-electron integral indicates the interaction between the electron distributions associated with electrons 1 and 2, respectively. We use g_{12} instead of r_{12}^{-1} because in the generalized form for $\overline{H}$ there may be additional operators of two-electron type besides just the familiar integrals. Such one- and two-electron quantitites further separated into one, two, and more atomic centers, are the quantitites that will have to be computed or in the case of simplified theories, approximated, to provide the results we require. At this point, we have an explicitly correlated, many-particle theory. It is important to distinguish this from an effective one-particle theory as in DFT or Hartree–Fock, which are much easier to apply to complicated systems.

To make this connection, we choose to reformulate the many-particle theory into an effective one-particle form. This is accomplished by insisting that the energy variation $\delta E = 0$, which means the derivative of E with respect to the orbitals that will compose the single determinant, $|\Phi\rangle$, vanish. As our expressions for $\mathrm{t}^{ab..}_{ij..}$, the CC equations, will depend upon the integrals over these orbitals, and consequently $\overline{H}$; this procedure is iterative. As any such variation of a determinant can be written in the form $|\Phi\rangle = \exp(\mathrm{T}_1)|0\rangle$, the single excitation projection of $\overline{H}$ has to vanish,

$$\langle^{a}_{i}|\overline{H}|0\rangle = 0 \tag{11}$$

$$= \langle a|\hat{h}_{T}|i\rangle \tag{12}$$

where we introduce the "transfer Hamiltonian" operator, $\hat{h}_T$. Since this matrix element vanishes between the occupied orbital, *i*, and the unoccupied orbital, *a*, we can use the resolution of the identity $1 = \sum_j |\mathrm{j}\rangle\langle j| + \sum_b |b\rangle\langle b|$ to rewrite this equation in the familiar form,

$$\hat{h}_T|i\rangle = \sum_j \lambda_{ji}|j\rangle = \epsilon_i|i\rangle \tag{13}$$

where the first form retains the off-diagonal Lagrangian multipliers, while the second is canonical. The above can equally well be done for HF-SCF theory, except $\hat{h}_T = \hat{f} = \hat{t} + \hat{v} + \hat{J} - \hat{K} = h + \hat{J} - \hat{K}$, where we have the kinetic-energy operator, the electron–nuclear attraction term $-\sum Z_A/|\mathbf{r} - \mathbf{R}_A|$, combined together into the one-particle element of Eq. (13); the Coulomb repulsion and the non-local exchange operator, repectively. The Hartree–Fock effective one-particle operator, $\widehat{J} - \widehat{K} = \sum_j \int d2\phi_j^*(2)(1 - P_{12})\phi_j(2)$, and there would be no correlation in the Fock operator. In that case, ϵ_i provides the negative of the Koopmans' estimate of ionization potentials, and ϵ_a the Koopmans' approximation to the electron affinities. For the *correlated* $\widehat{h}_T$, which is the one-particle theory originally due to Brueckner [45, 46], all single excitations vanish from the exact wavefunction, and as a consequence, we have maximum overlap of the Brueckner determinant with the exact wavefunction, $|\langle\Phi_B|\Psi\rangle|$. In general, Brueckner theory is not Hermitian, but in any order of perturbation theory we can insist upon its hermiticity, i.e., $\langle i|\widehat{h}_T|a\rangle = 0$, and that will be sufficient for our purposes.

The specific form for the transfer Hamiltonian matrix element is

$$\langle a|\widehat{h}_T|i\rangle = \langle a|\widehat{f}|i\rangle + \frac{1}{2}\left[\langle aj||cb\rangle t_{ij}^{cb} - \langle kj||ib\rangle\, t_{kj}^{ab}\right] \tag{14}$$

where summation over repeated indices is implied.

Keeping the form of the $\widehat{h}_T$ operator in the $\langle a|\widehat{h}_T|i\rangle$ matrix element the same, when a is replaced by an occupied orbital, m, we have

$$\langle m|\widehat{h}_T|i\rangle = \langle m|\widehat{f}|i\rangle + \frac{1}{2}\left[\langle mj||cb\rangle t_{ij}^{cb} - \langle kj||ib\rangle t_{kj}^{mb}\right] \tag{15}$$

Then, we have the Hartree–Fock-like equations but now for the correlated one-particle operator, $\widehat{h}_T$, represented in the basis set, $|\chi\rangle$, where $\mathbf{S} = \langle\chi|\chi\rangle$ is the overlap matrix,

$$\mathbf{h}_T\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon \tag{16}$$

and the (molecular) orbitals are $|\phi\rangle = |\chi\rangle\mathbf{C}$. The Brueckner determinant, Φ_B, is composed of the lowest n occupied MOs, $|\phi_0\rangle = |\chi\rangle\mathbf{C}_0$ In particular, the matrix elements for the transfer Hamiltonian in terms of the atomic orbital basis set are

$$\langle\mu|h_T|\nu\rangle = \left[\overline{h}_\nu^\mu + P_\alpha^\beta(\overline{g}_{\nu\beta}^{\mu\alpha} - \overline{g}_{\beta\nu}^{\mu\alpha})\right] \tag{17}$$

$$P_\mu^\nu = c_\mu^i c_i^\nu \tag{18}$$

(summation of repeated indices is assumed),where P_μ^ν is the density matrix for the Brueckner determinant. Hence, subject to modified definitions for $\overline{h}_\nu^\mu$ and $\overline{g}_{\nu\beta}^{\mu\alpha}$, which we will assume are renormalized to include the critical parts of the three- and higher-electron effects, we have the matrix ϵ which contains the exact ionization potentials for the system.

The total energy,

$$
\begin{aligned}
E &= \langle \Phi_B | \overline{H} | \Phi_B \rangle \\
&= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle + \frac{1}{4}\sum_{i,j,a,b}\langle ij||ab\rangle t_{ij}^{ab} \qquad (19)\\
&= \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j}\langle ij|\overline{g}_{12}|ij\rangle \qquad (20)\\
&= \frac{1}{2} Tr\mathbf{P}(\overline{\mathbf{h}}+\overline{\mathbf{h}}_T^{\prime}) \qquad (21)
\end{aligned}
$$

$$
\overline{g}_{12} = r_{12}^{-1} + \frac{1}{2}\sum_{a,b} T_2||ab\rangle\langle ab|| \qquad (22)
$$

is also written in terms of the *reference* density matrix $\mathbf{P} = \mathbf{C}_0\mathbf{C}_0^{\dagger}$, evaluated from the occupied orbital coefficients, $\mathbf{C}_0$. The quantityt $\overline{\mathbf{h}}_T^{\prime} = \epsilon^{\prime}$differs from the form in Eq. (15), because of the absence of the third term on the RHS. This term is an orbital relaxation term that only pertains to the ionization potentials, as there we would need to allow the system to relax after the ionization. Hence, this cannot contribute to the ground state energy, and its manifestation of that is that the total energy cannot be written in terms of the exact ionization potentials in Eq. (13), but can be written in terms of an approximation introduced by $\overline{\mathbf{h}}_T^{\prime}$. The analytical forces for MD can be written easily, as well. Notice $\widehat{\mathbf{h}}_T$ includes all electron correlation. Once $\overline{h}_{\nu}^{\mu}$ and $\overline{g}_{\nu\beta}^{\mu\alpha}$ are specified, which need to be viewed as quantities to be determined *to reproduce the reference results from ab initio correlated calculations*, we obtain self-consistent solutions for the correlated, effective, one-particle Hamiltonian. The self-consistency is essential in accounting for bond-breaking and associated charge rearrangement.

The overlap matrix is included for generality, but as is often done in NDDO type theories, enforcing the ZDO approximation removes it. Another way to view this is to assume the parameters are based upon using the orthonormal expansion basis, $\overline{|\chi\rangle} = |\chi\rangle\mathbf{S}^{-1/2}$ which gives $\overline{\mathbf{h}}_T = \mathbf{S}^{-1/2}\mathbf{h}_T\mathbf{S}^{-1/2}$. Developing this expression to include low-order in some $\mathbf{S}$ terms permits us to still retain the simpler and computationally faster orthogonal form of the eigenvalue equation, yet introduce what is sometimes called “Pauli repulsion” in the semi-empricial community [22]. A self-consistent solution provides the coefficients, $\mathbf{C}$ and the *reference* orbital energies, $\epsilon^{\prime}$,which as we discussed, are not the exact Ip’s that would come from including the contributions of the t_{jk}^{mb} amplitudes, which contain three-hole line and one-particle line. Such terms arise in the generalized EOM or Fock space CC theory for ionized, electron attached, and excited states. In lowest order, $t_{jk}^{mb} = \langle mb||jk\rangle/(\epsilon_j + \epsilon_k - \epsilon_b - \epsilon_m)$.

4. Transfer Hamiltonian: Density Functional Viewpoint

The DFT approach to the $\hat{h}_T$ starts from a different premise that is actually simpler, since DFT is already exact in an independent particle form, unlike the usual many-particle theory above. As is well known, we have the Sham one-particle Hamiltonian [32] whose first n eigenvectors give the exact density,

$$\hat{h}_S = \hat{t} + \hat{v} + \hat{J} + \hat{V}_x + \hat{V} \tag{23}$$

$$\hat{h}_S|i\rangle = \epsilon_i|i\rangle. \tag{24}$$

$$\mathbf{h}_S\mathbf{C} = \mathbf{SC}\epsilon \tag{25}$$

$$\rho(1) = \sum_i \phi_i(1)\phi_i^*(1) = \sum_{\mu,\nu} \chi_\mu(1)P_{\mu\nu}\chi_\nu^*(1) \tag{26}$$

and like the above, the density matrix is $\mathbf{P} = \mathbf{C}_0\mathbf{C}_0^\dagger$. The highest-occupied MO, n, has the property that $\epsilon_n = -\mathrm{Ip}(n)$. However, solving these equations does not provide an energy until we know the functional $E_{xc}[\rho]$, from which we know that $\delta E_{xc}[\rho]/\delta\rho(1) = V_{xc}(1)$, to close the cycle. The objective of DFT is to get the density, ρ, first; and then all other ground state properties follow; in particular, the energy and forces we need for MD. The transfer Hamiltonian in this case will be defined by the condition that $\rho_{\mathrm{CCSD}} = \rho_{\mathrm{KS}}$. Satisfying this condition means that we could obtain a V_{xc} from this density by using the ZMP method [47], but our approach is simply to parameterize the elements in $\hat{h}_S = \hat{h}_T$ in analogy with that in semi-empirical quantum chemistry or TB such that the density condition is satisfied. This should specify V_{xc}, and indeed, the other terms in $\hat{h}_T$, which is then sufficient to obtain the forces, $\{\partial E(\mathbf{R})/\partial \mathbf{X}_A\}$. Note this bypasses the need to use an explicit $\mathrm{E}_{xc}[\rho]$,but, of course, that would always be an option. We can also bypass any explicit treatment of the kinetic energy operator by virtue of parametrization of $\hat{h} = \hat{t} + \hat{v}$ as in the semi-empirical approach discussed below. Besides the density condition, we also have the option to use the force condition in the sense that the forces can be obtained from CC theory, and then their values directly used to obtain the parameterized version of $\hat{h}_S = \hat{h}_T$. Ideally, the parameters will be able to describe both the densities and the forces, although this raises the issue of the long-term inability of semi-empirical methods to describe structures and spectra with the same parameters, discussed further in the last section.

As our objective is to be able to define a $\hat{h}_T$ that will satisfy many of the essential elements of *ab initio* theory, some of interest besides the forces are the density, and the ionization potential and electron affinity. The latter define the Mulliken electronegativity, $E_N = (I - A)/2$, which should help to ensure that our calculations correctly describe the charge distribution in a system and the density. We also know the correct long-range behavior of the density is determined by the homo ionization potential, $\rho\,(r) \propto \exp(-2\sqrt{2I})r$, which is a property of exact DFT. If the density is right, then we also know that we will get the correct dipole moments for the molecules involved, and this is likely to be critical if we hope to correctly describe polar systems like water, along with their hydrogen bonding.

5. What About Semi-Empirical Methods?

Before embarking upon a particular form for the transfer Hamiltonian that must inevitably be semi-empiricial or TB type, we can ask what kind of accuracy is possible with such methods. In an recent paper on PM5, a parameterized NDDO Hamiltonian, [20, 21] Stewart reports that the PM5 heats of formation for over ∼1000 molecules composed of H, C, N, O, F, S, Cl, Br, and I have a mean absolute deviation (MAD) of 4.6 kcal/mol, nearly the same as DFT using BLYP or BPW91. The errors of PM3 are slightly larger (5.2) and AM1 (7.2). The largest errors are 27.2, (PM5), 35.1, (PM3), 54.8, (AM1) and 55.7 for BLYP and 34.5 for BPW91. Using a TZ instead of a DZ basis for the latter gives some improvement in the worst cases. For Jorgensen's reparameterized PM3 and MNDO methods, referred to as PDDG [22, 25], the MAD heats of formation for 662 molecules limited to H, C, N, and O are reduced from 8.4 to 5.2, and with some extra PDDG additions, from 4.4 to 3.2 kcal/mol. For geometries, PDDG gets bond lengths to a MAD of 0.016 Å, 2.3° bond angle, and 29.0° dihedral angle. The principal Ip is typically within ∼0.5 eV – though it can be off by several – which is some 3% more accurate than PM3 and 12% less accurate than PM5. For dipole moments, the MAD is 0.24 Debye. There is less information about transition states and activation barriers, but these methods have seen extensive use for such problems in chemistry.

Recent TB work termed SCC-DFTB for self-consistent charge density functional TB [11] is based upon DFT rather than HF and is less empirical, but still simplified using similar approximations for two-center interactions as in NDDO, discussed below. It is developed for solids as well as molecules. For the latter, in 63 organic examples the MAD deviations in bond lengths are 0.012 Å, and angles, 1.80°. For heats of reaction, in 36 example molecules composed of H, C, N, O the MAD is 12.5 kcal/mol compared to 11.1 for DFT-LSD. On the other hand, we can have dramatic failures. None of these *new* semi-empirical methods yet even treat Si, much less heavier elements of the sort that are important in many materials applications. To quote just one example, in comparisons of nine Zn complexes with B3LYP and CCSD(T), "MNDO/d failed the case study" and the errors compared to *ab initio* or DFT were dramatic." The authors [48] say "No one semiempiricial model is applicable for the calculations of the whole variety of structures found in Zn chemistry."

6. Forms for Tranfer Hamiltonian

Our objective is to model $\widehat{h}_T$ for the particular phenomena of interest and for chosen representative systems (i.e. unlike normal semi-empirical theory we *do not* expect the parameters to describe many elements at once) in a way that permits the routine, self-consistent treatment of a very large number of the same kinds of atoms. We also recognize that the traditional approaches are built upon approximating the HF-SCF one-particle Hamiltonian, $\widehat{f}$, not the more exact DFT or Brueckner approach discussed above. Also, traditionally, only a minimum basis set of an s orbital on H, and one s and a set of p orbtials are used on the other atoms, until d orbtials are occupied. Thinking more like *ab initio* theory, we do not presuppose such restrictions, but will use polarization functions and potentially double zeta sets of s and p orbitals on all atoms. We recognize the attraction of a transfer Hamiltonian that (1) consists solely of atomic parameters; and (2), is essentially two-atom in form, as all three- and four-center contributions are excluded. This is the fundamental premise of all neglect of differential overlap approximations [15, 17, 19]. Hence, as a first realization, guided by many years of semi-empirical quantum chemistry, we choose the "neglect of diatomic differential overlap" (NDDO) Hamiltonian,

$$\begin{aligned}\langle\mu|\widehat{h}_T|\nu\rangle = {} & \sum_{\mu\in A}\alpha_{\mu\nu}\delta_{u\upsilon} + \sum_{\substack{\mu=\alpha,\nu=\beta\\ \mu,\nu\in A}} P_\alpha^\beta\overline{(\mu\alpha|\nu\beta)} - \sum_{\substack{\mu\beta=\nu\alpha,\mu\neq\beta\\ \mu,\beta\in A}} P_\alpha^\beta\overline{(\mu\beta|\nu\alpha)}\\ & + \sum_{\mu\in A,\nu\in B}\frac{1}{2}(\beta_u+\beta_\upsilon)S_\nu^\mu + \sum_{\substack{\mu=\alpha\in A,\upsilon,\beta\in B,\\ \nu=\beta\in B,\mu,\alpha\in A}} P_\alpha^\beta\overline{(\mu\alpha|\nu\beta)}\\ & - \sum_{\substack{\mu\neq\beta\in A,\\ \nu\neq\alpha\in B}} P_\alpha^\beta\overline{(\mu\beta|\nu\alpha)} \end{aligned} \tag{27}$$

consisting of atomic and diatomic units. $\alpha_{\mu\mu}$ is a purely atomic quantity that represents the one-particle part of the energy of an electron in its atomic orbital. We would have different values for s, p, d,... orbitals, collectively indicated as α_A. The one-center, two-electron terms for atom A are separated into coulomb and exchange terms and weighted by the density matrix. No explicit correlation operator as in DFT is yet considered. Instead modifications (parameterizations) of the coulomb and exchange terms are viewed as potentially accomplishing the same objective. β_u is an atomic parameter indicative of each orbital type (s,p,d) on atom A and S_ν^μ is the overlap integral between, formally, two atomic orbitals on atoms A and B. A Slater type orbital on atom A is $\chi_\text{A}=r_\text{A}^{n-1}\exp(-\zeta_\text{A})Y_{l,m}(\vartheta_\text{A},\varphi_\text{A})$, and the overlap integral, $\text{S}_\nu^\mu(\zeta_\text{A},\zeta_\text{B})$ depends upon ζ_A and ζ_B, so it is entirely determined by what the atoms are. So it, too, consists of atomic parameters.

The terms which include density matrix elements account for the two-electron repulsion terms which depend upon the purely one-center two-electron integral type, $\overline{(\mu_{\mathrm{A}}\nu_{\mathrm{A}}|\mu_{\mathrm{A}}\nu_{\mathrm{A}})} = \gamma_{\mathrm{AA}}^{\mu\nu}$. A typical choice for the two-center, two-electron term then becomes [49, 50]

$$\overline{(\mu_{\mathrm{A}}\nu_{\mathrm{A}}|\mu_{\mathrm{B}}\nu_{\mathrm{B}})} \propto \left[r_{\mathrm{AB}}^2 + (c_{\mathrm{A}}^{uv} + c_{\mathrm{B}}^{uv})^2\right]^{-1/2} \tag{28}$$

where $r_{\mathrm{AB}} = R_{\mathrm{AB}} + q_i$ and the additive terms c^{uv} are numerically determined such that the two-center repulsion integral goes to the proper one-center limiting value. R_{AB} is the distance bewteen atoms A and B, but differs from r_{AB} due to the multipole method used to compute the two-electron integral. For $(s_{\mathrm{A}}s_{\mathrm{A}}|p_{\mathrm{B}}p_{\mathrm{B}})$, a monopole and quadrupole are used for the p electron distribution while a monopole is used for the s distribution. The radial extent of the multipoles is given by $q_i = q_{pB,}$ and is a function of the atomic orbital exponent ζ_{B} on atom B. This form for the two-electron integrals assumes the correct long-range $(1/R)$ behavior. More general forms for the two-center, two-electron integrals combine such contributions together from several multipoles to distingush $\overline{(ss|ss)}$ from $\overline{(ss|dd)}$, etc. [19, 51]. This set of approximations defines the NDDO form of the matrix elements of $\widehat{h}_T$ between two atomic orbitals.

Now we have to consider the nuclear repulsion contribution to the energy, $\sum_{\mathrm{A,B}}\mathrm{Z_A Z_B}/R_{\mathrm{AB}}$. Importantly, and unlike in *ab initio* theory, the effective atomic number, $\mathrm{Z_A}$,which is chosen initially to be equal to the number of valence electrons being contributed by atom A, is also made a function of all $\mathrm{R_{AB}}$ in the system. This introduces several new parameters into the calculation, justified roughly by some ideas of electron screening. The AM1 choice [16] for the latter reflects screening of the effective nuclear charge with the parameterized form

$$\begin{aligned} E_{\mathrm{CR}} = {} & Z_{\mathrm{A}}' Z_{\mathrm{B}}' \overline{(s_{\mathrm{A}}s_{\mathrm{A}}|s_B s_{\mathrm{B}})} \left\{1 + e^{(-d_{\mathrm{A}}R_{\mathrm{AB}})} + e^{(-d_{\mathrm{B}}R_{\mathrm{AB}})}\right\} \\ & + \frac{Z_{\mathrm{A}}' Z_{\mathrm{B}}'}{R_{\mathrm{AB}}} \left\{\sum_k a_{\mathrm{A}k} e^{-b_{\mathrm{A}}(R_{\mathrm{AB}} - C_{k\mathrm{A}})^2} + \sum_k a_{\mathrm{B}k} e^{-b_{\mathrm{B}}(R_{\mathrm{AB}} - C_{k\mathrm{B}})^2}\right\} \end{aligned} \tag{29}$$

These core repulsion (CR) parameters, d, b, a and C account for the nuclear repulsion, which means they contribute to total energies and forces, but not to purely electronic results. The latter depend upon the *electronic parameters* $\beta_{\mathrm{A},}\gamma_{\mathrm{AA}}, \alpha_{\mathrm{A}}, \ldots$. In our work, both sets are specified via a genetic algorithm to ensure that correlated CCSD results are obtained for representative systems, tailored to the phenomena of interest.

Looking at the above approximations, we see that we retain only one and two-center two-electron integrals. In principle, we can have a three-center one-electron integral from $\langle\mu_{\mathrm{A}}|Z_{\mathrm{C}}/|\mathbf{r} - \mathbf{R}_{\mathrm{C}}\|\nu_{\mathrm{B}}\rangle$, but in NDDO, such terms are excluded as well. Any approximation of $\widehat{h}_T$ that is to be tied to *ab initio* results, has to have the property of “saturation.” To achieve this, we insist that our form for $\widehat{h}_T$ be fundamentally short range. We see from the above, that our $\widehat{h}_T$ depends on two-center interactions, but unlike TB, not just those for the nearest neighbor atoms but for all the two-body interactions in the system. This short-range character helps to saturate the atomic parameters for comparatively small example systems that are amendable to *ab initio* correlated methods. Then once the atomic parameters are obtained, and found to be unchanged to within a suitable tolerance when redetermined for larger clusters, they define a saturated, self-consistent, correlated, effective one-particle Hamiltonian that can be readily solved for quite large systems to rapidly determine the forces required for MD. We also have easy access to the second-derivatives (Hessians) for definitive saddle point determination, vibrational frequencies, and interpolation between calculations at different points for MD.

Using H_2O as an example for saturation, we can obtain the cartesian force matrix for the monomer by insisting that our simplified Hamiltonian provide the same force curves as a function of intra-atomic separation for breaking the O–H bond with the other degrees of freedom being optimum (i.e. a distinguished reaction path). Call this matrix $F_{\mathrm{A.}}$ From F_{A} we use a GA to obtain the Hamiltonian parameters that, in turn, determine $\overline{h}$ and $\overline{g}$ elements that make our transfer Hamiltonian reproduce these values. The more meaningful gradient norm $|F\ |$ is used in practice rather than the individual cartesian elements. Now consider two water molecules interacting. The principal new element is the dihedral angle that orients one monomer relative to the other, but the H-bonding and dipole–dipole interaction will cause some small change when we break an O–H bond in the dimer. Our first approximation to $F_{\mathrm{AB}}=F_{\mathrm{A}}+F_{\mathrm{B}}+V_{\mathrm{AB}}$. Then by changing our parameters to accomodate the dimer bond breaking, we get slightly modified $\overline{h}$ and $\overline{g}$ elements in the transfer hamiltonian. This makes $\mathrm{F}_{\mathrm{AB}} = F'_{\mathrm{A}} + F'_{\mathrm{B}}$. Going to a third unit, we would add $V'_{\mathrm{ABC,}}\,V'_{\mathrm{AC,}}\,V'_{\mathrm{BC}}$ perturbations and repeat the process to define $F_{\mathrm{ABC}} = F''_{\mathrm{A}} + F''_{\mathrm{B}} + F''_{\mathrm{C}}$. Since these atomic based interactions will rapidly fall off with distance, we expect that relatively quickly we would have a saturated set of parameters for the bond breaking in water with a relatively small number of clusters. We can obviously look at other properties, too, such as dipole moments, cluster structures, etc., to assess their degree of saturation with our $\widehat{h}_T$ parameters. If we fail to achieve a satisfactory saturation, then we have to pursue more flexible, or more accurate forms of transfer Hamiltonians. It is essential to identify the terms that matter, and the DFT form provides complimentary input to the wavefunction approach in this regard. Also, unlike most semi-empirical methods we do not limit ourselves to a minimum basis set. The general level we would anticipate is CCSD with a double-zeta + polarization basis, while dropping the core electrons. This is viewed as the quality of *ab initio* result that we would pursue for complicated molecules.

In addition, following the equation-of-motion (EOM) CC approach [52], we insist that

$$\overline{H}\widehat{R}_k|0\rangle = \omega_k\widehat{R}_k|0\rangle \tag{30}$$

where $\widehat{R}_k \exp(T)|0\rangle = \Psi_k$ and ω_k is the excitation energy for any ionized, $I_{k,}$ electron-attached, $A_{k,}$ or excited state. In other words, this provides Ips and Eas that tie to the Mulliken electronegativity, to help to ensure that our transfer Hamiltonian represents the correct charge distribution and density size. Furthermore, whereas forces and geometries are highly sensitive to the core-repulsion parameters, properties like I and A are sensitive to the electronic parameters in the transfer Hamiltonian.

The transfer Hamiltonian procedure is far more general than the particular choice of Hamiltonian chosen here, since we can choose any expansion of $\overline{H}$ or $\widehat{h}_T$ that is formally correct and include elements to be computed or parameters to be determined, to define a transfer Hamiltonian. Furthermore, we can insist that it satisfy suitable exact and consistency conditions such as having the correct asymptotic or scaling behavior. Other desirable conditions might include the satisfaction of the virial and Hellman–Feynman theorems. We can also choose to do many of the terms like the one-center ones, *ab initio,* and keep those values fixed subsequently. Then, our simplified forms $\frac{1}{2}(\beta_u + \beta_v)S_v^{\mu}$ and that of Eq. (29), are the only ones where there is an electronic dependence upon geometry. Adding this dependence to that from the core–core repulsions, has to provide the forces that drive the MD. We can explore many other practical approximations such as supressing self-consistency by setting $\mathbf{P} = \mathbf{1}$**,** and impose the restriction that only *nearest neighbor* two-atom interactions be retained, to extract a non-self-consistent TB Hamiltonian that should be very fast in application. We can obviously make many other choices and create, perhaps, a series of improving approximations to the *ab initio* results that parallel their computational demands.

7. Numerical Illustrations

As an illustration of the procedure, consider the prototype system for an Si–O–Si bond as in silica, pyrosilicic acid (Fig. 6). This molecule has been frequently used as a simple model for silica. We are interested in the Si-O bond rupture. Hence, we perform a series of CCSD calculations as a function of the Si–O distance all the way to the separated radical units, $\cdot$Si(OH)$_3$ and $\cdot$O–Si(OH)$_3$, relaxing all other degrees of freedom at each point (while avoiding any hydrogen bonding which would be artificial for silica) using now well-known CC analytical gradient techniques [36]. For each point we compute the

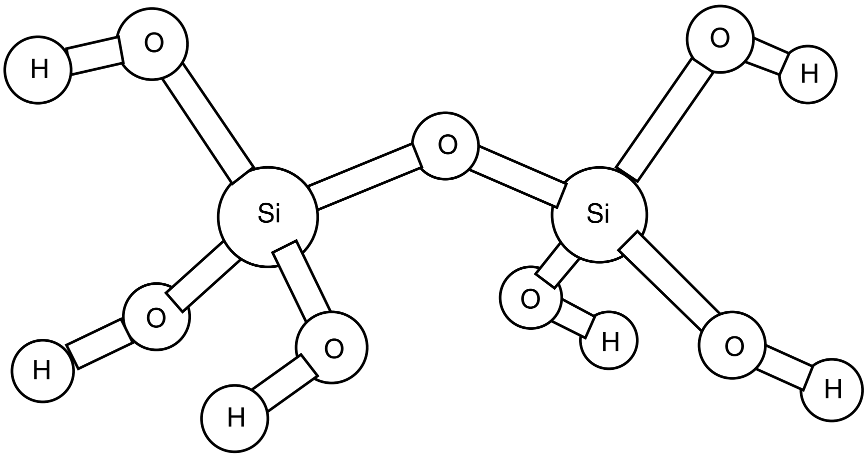

Figure 6. Structure of pyrosilicic acid.

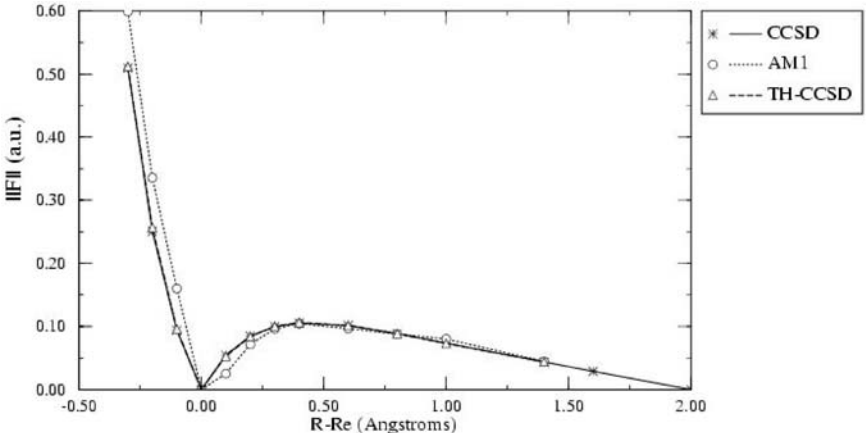

Figure 7. Comparison of forces from standard semi-empirical theory (AMI) and the transfer Hamiltonian (TH-CCSD) with coupled-cluster (CCSD) results for dissociation of pyrosilicic acid into neutral fragments.

gradient norm of the forces for the $3N$ cartesian coordinates, q_I, (3 per atom A), $|F| = \sum_I^{3N}[(\partial E/\partial q_I)^2]^{1/2}$ and use the genetic algorithm PIKAIA [53] to minimize the difference between |F(CCSD)-F($\widehat{h}_T$)| for the transfer Hamiltonian and the CCSD solution. This is shown in Fig. 7. Since forces drive the MD, their determination is more relevant for the problem than the potential energy curves, themselves. For this case, we find that fixing the parameters in our transfer Hamiltonian that are associated with the core-repulsion function is sufficient, leaving the electronic parameters at the standard values for the AM1 method. As seen in Fig. 7, these new parameters are responsible for removing AM1s too large repulsion at short Si–O distances and erroneous behavior shortly beyond the equilibrium point. Hence, to a small tolerance, the transfer Hamiltonian provides the same forces as that in the highly sophisticated *ab initio* CCSD method.

In a second study, QM forces permit the description of different electronic states. As an example, for this system we can also separate pyrosilicic acid into charged fragments, Si(OH)3^{+} and O–Si(OH)3^{-}, and in a material undergoing bond-breaking, we would expect to take multiple paths such as this. A classical potential has no such capability. Figure 8 shows the curve and once again we obtain a highly accurate representation from the transfer Hamiltonian, *with the same parameters obtained for the radical dissociation.* Hence, our transfer Hamiltonian has the capability of describing the effects of these different electronic states in simulations, which besides enabling reliable descriptions of bond-breaking, should have an essential role if a materials' optical properties are of interest. Figure 9 shows the integrated force curves to illustrate that even though the parameters were determined from the forces, the associated potential energy surfaces are also accurate compared to the reference CCSD results, and more accurate than the conventional AM1 results. The latter has an error of ~0.4 eV between the neutral and charged paths compared to the CCSD results. We have also investigated the parameter saturation. Moving to trisilicic acid we obtain the reference results wihout any further change in our parameters.

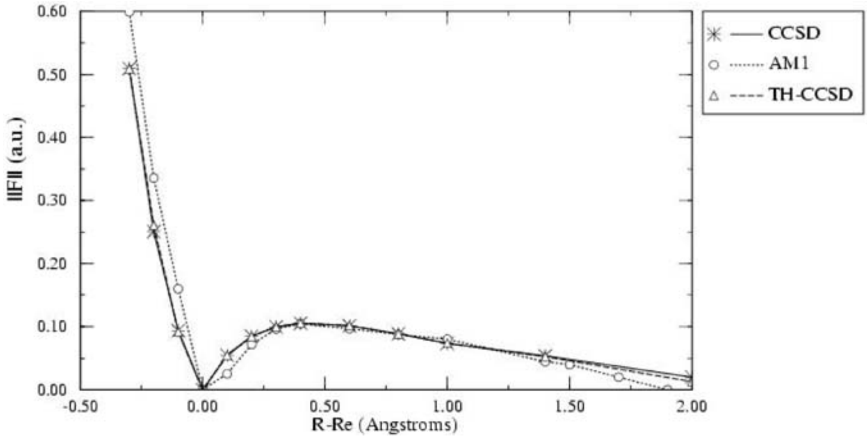

Figure 8. Comparison of forces from standard semi-empirical theory (AM1) and the Transfer Hamiltonian (TH-CCSD) with coupled-cluster (CCSD) results for dissociation of pyrosilicic acid into charged fragments.

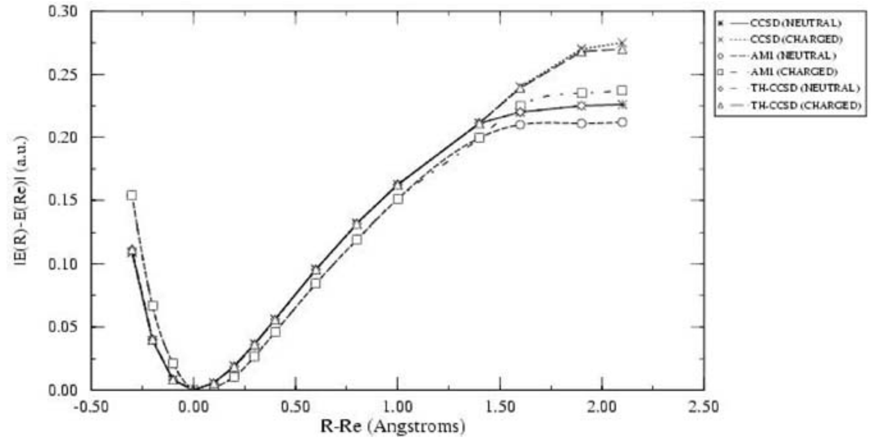

Figure 9. Comparison of PES for dissociation of pyrosilicic acid. Each curve is labeled by the Hamiltonian used and the dissociation path followed.

The correct description of complicated phenomena in materials requires that the approach be able to describe, accurately, a wealth of different valence states and coordination states of the relevant atoms involved. For example, the surface structure of silica is known to show three, four, and five coordinate Si atoms. Hence, a critical test of the ability of the $\widehat{h}_T$ is how well its form can account for the observed structure of such species *with the same parameters already determined for bond breaking.* In Figs. 10 and 11, we show comparisons of the $\widehat{h}_T$ results for some $\mathrm{Si}_x\mathrm{O}_y$ molecules with DFT (B3LYP), various two-body classical potentials [54, 55], and a three-body potential [56] frequently used in simulations, and molecular mechanics [26]. The reference values are from CCSD(T), which are virtually the same as the experimental values when available. The $\widehat{h}_T$ results are competitive with DFT and superior to all classical forms, including even MM with standard parameterization. The latter is usually quite accurate for molecular structures at equilibrium geometries, but not necessarily for SiO_2. MM methods do not attempt to describe bond breaking.

The comparative timings using the various methods are shown in Table 2 for two different sized systems, pyrosilicic acid and a 108-atom SiO_2 nanorod [57]. The 216-atom version is shown in Fig. 12.

The $\widehat{h}_T$ procedure is about 3.5 orders of magnitude faster than the gaussian basis B3LYP DFT results, which is another ~3.5 orders of magnitude faster than CCSD[ACESII]. The 108 atom nanorod is clearly well beyond the capacity of CCSD *ab initio* calculations, but even the DFT result (in this case with a plane wave basis using the BO-LSD-MD (GGA) program, is excessive, while the $\widehat{h}_T$ is again three to four orders of magnitude faster. With streamlining of programs, we expect that this can still be significantly improved.

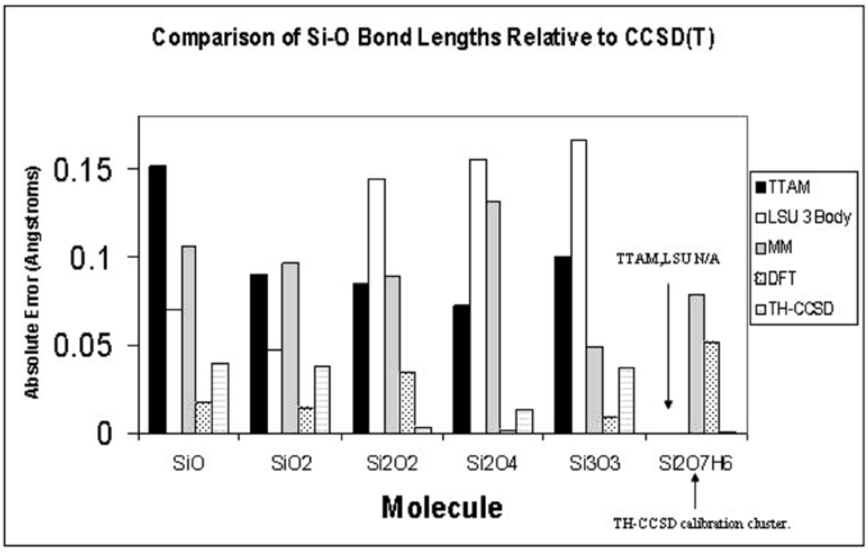

Figure 10. Error in computed Si_xO_y equilibrium bond lengths relative to CCSD(T) using various potentials.

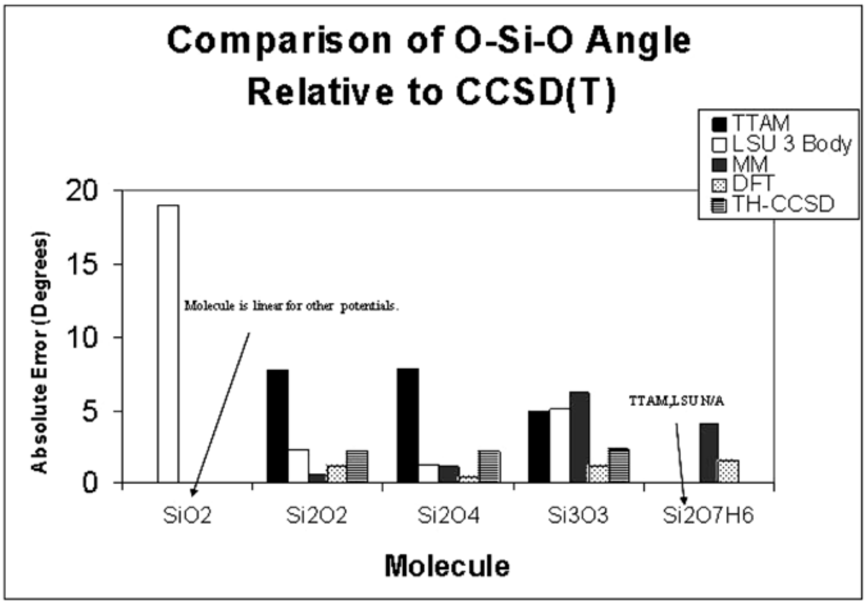

Figure 11. Error in computed Si_xO_y equilibrium bond angles relative to CCSD(T) using various potentials.

Table 2. Comparative timings for electronic structure calculations (IBM RS/6000)

Pyrosilicic acid		108-atom nanorod	
Method	CPU time (s)	Method	CPU time (s)
CCSD	8656	CCSD	N/A
DFT	375	DFT	85,019
$\widehat{h}_T$	0.17	$\widehat{h}_T$	43
BKS	0.001	BKS	0.02

Finally, to illustrate the results of a simulation we consider the 216-atom SiO_2 system of Fig. 12, subject to a uniaxial stress, using various classical potentials and that for our QM transfer Hamiltonian. The equilibrated nanorod was subjected to uniaxial tension by assigning a fixed velocity (25 m/s) in the loading direction to the 15 atoms in the caps at each end of the rod. The stress was computed by summing the forces in the end caps and dividing by the projected cross sectional area at each time step. The simulations evolved for (approximately) 10 ps where the system temperature was maintained at 1 K by velocity rescaling.

Figure 13 shows the computed stress–strain curves. The main differences between the classical potentials and their QM potentials seems to be the differnce at the maximum and the long tail indicating surface reconstruction. The QM potential shows the expected brittle fracture, perhaps a little more than the classical potentials. The transfer Hamiltonian, retains self-consistency, state specificity, and permits readily adding other molecules to simulations after ensuring that they, too, reflect the reference *ab initio* values for their various interactions. Hence, the transfer Hamiltonian built upon NDDO or more general forms, would seem to offer a practical approach to moving toward the objective of predictive simulations.

In Fig. 14 we show the same kind of information about bond-breaking in water, showing the substantial superiority of the $\widehat{h}_T$ results compared to standard AM1. A well-known failing of semi-empirical methods is their inability to correctly describe H-bonding. In Fig. 15 we compare the equilibrium structure of the water dimer obtained from the $\widehat{h}_T$, *ab initio* MBPT(2), and standard semi-empirical theory. It provides the quite hard to describe water dimer in excellent agreement with the first-principles calculations, contrary to AM1 which leads to errors in the donor–acceptor O–H bond of 0.15 Å. In this example, we have to change the electronic parameters along with the core-core repulsion. We would expect this to be the case for most applications. In the future, we hope we can develop the $\widehat{h}_T$ to the point that we will have an accurate, QM, description of water *and its interactions* with other species.

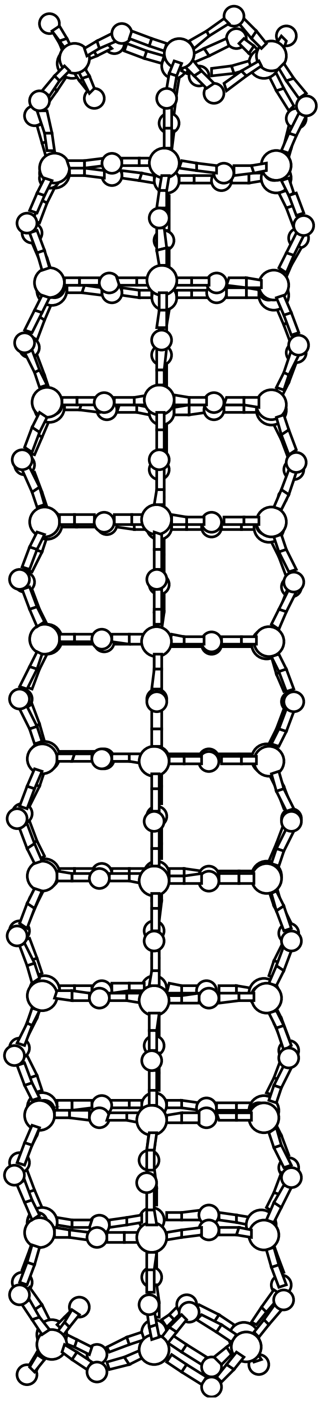

Figure 12. Silica nanorod containing 216 atoms.

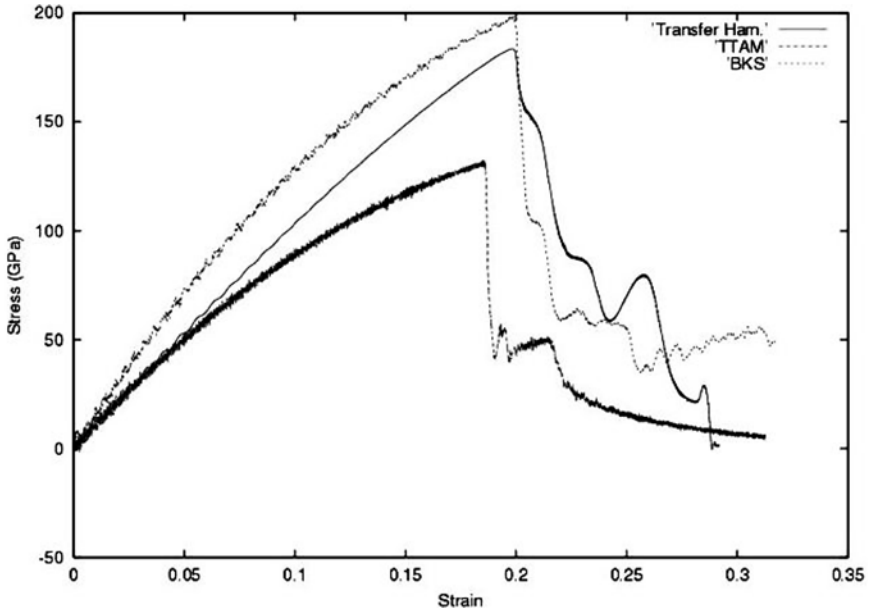

Figure 13. Stress–strain curve for 216-atom silica nanorod with classical and quantum potentials.

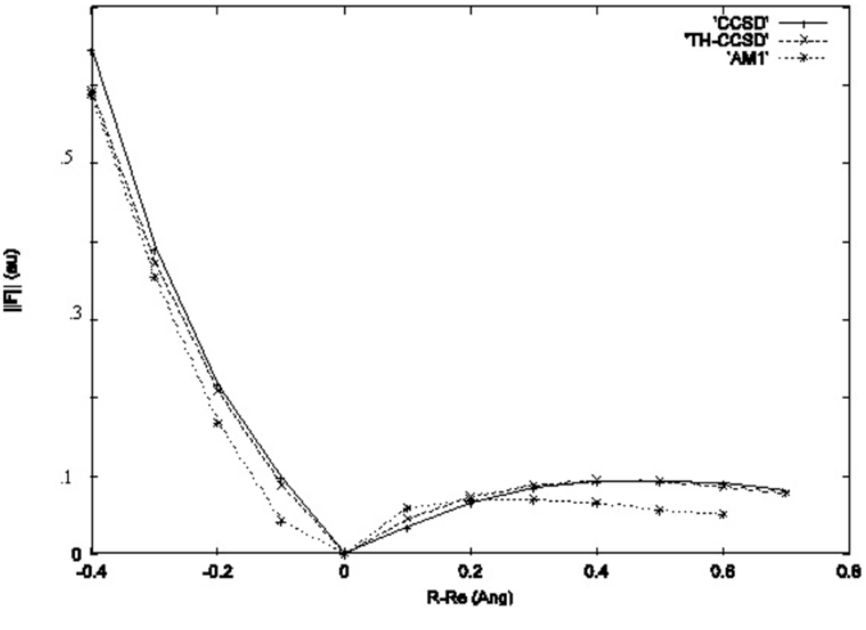

Figure 14. Comparison of forces for O–H bond breaking in water monomer.

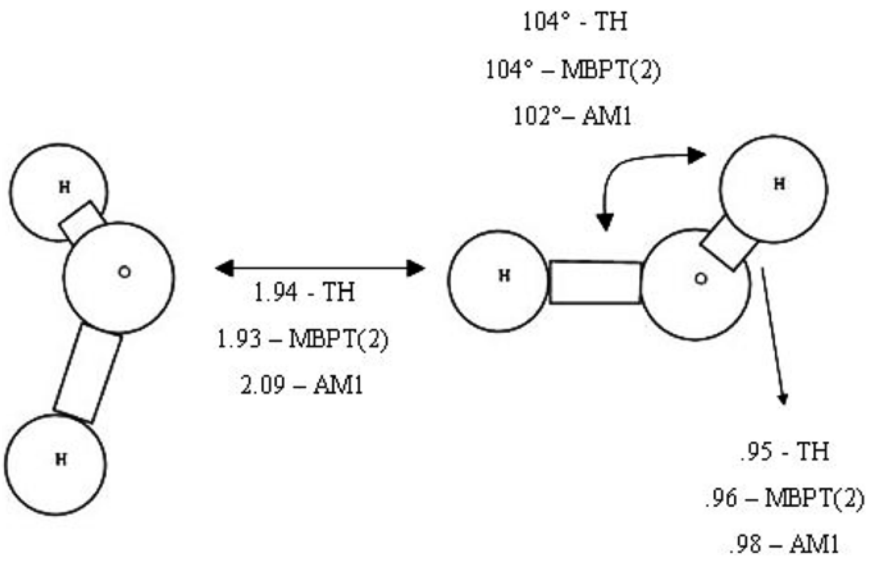

Figure 15. Structure of water dimer using transfer Hamiltonian, MBPT(2), and standard AM1 Hamiltonian. Bond lengths in angstroms and angles in degrees.

8. Future

This article calls for some expectations for the future. We have little doubt that the future will demand QM potentials and forces in simulations. It seems to be the single most critical, unsolved, requirement if we aspire toward "predictive" quality. If we could use high-level CC forces in simulations for realistic systems, we would be as confident of our results – as long as the phenomena of interest is amendable to classical MD – as we would be for the determination of molecular properties at that level of theory and basis. Of course, in many cases we cannot run MD for long enough time periods to allow some phenomena to manifest themselves, perhaps forcing more of a kinetic Monte Carlo time extension at that point. We clearly also need much accelerated MD methods regardless of the choice of forces.

Like the above NDDO and TB methods, DFT as used in practice, is also a "semi-empirical" theory, as methods like B3LYP now use many parameters to define their functionals and potentials. Even the bastion of state-of-the-art *ab initio* correlated methods – coupled-cluster theory – is not exact because it depends upon a basis set, as shown in the examples in the introduction. Since even DFT cannot generally be used in MD simulations involving more than $\sim$300 atoms, to make progress in this field demands that we have "simplified" methods that we can argue retain *ab initio* or DFT accuracy but now for

>1000 atoms, and that can be readily tied to simulations. In this article, we have suggested a procedure for doing so. We showed that the many-electron CC theory could be reformulated into a single determinant form, but at the cost of having a procedure to reliably introduce the quantites we called g_{μ}^{ν}, $g_{\mu\nu}^{\lambda\delta}$, $g_{\mu\nu\epsilon}^{\lambda\delta\eta}$, etc. These are complicated quantities that in an *ab initio* calculation would depend upon one- and two-electron integrals over the basis functions and the cluster amplitudes in $\widehat{T}$. We could directly compute these elements from *ab initio* CC methods, to assess their more detailed importance and behavior, and expect to do so. But we prefer, initially, to obtain most of these elements from consideration of a smaller set of quantities and parameters like those in NDDO, or perhaps in TB; and investigate whether those limited numbers of parameters will be capable of fixing $\widehat{h}_T = \sum_{\mu,\nu} |\mu\rangle\langle\mu|\widehat{h}_T|\nu\rangle\langle\nu|$ to the required accuracy. We believe in ensuring that $\widehat{h}_T$ has the correct long- and short-range behavior, including the united atom and the separated atom limits. We also want to make sure that the proper balance between the core–core repulsions and the electronic energy is maintained. In our opinion, this is the origin of the age-old problem in semi-empirical theory, that there needs to be different parameters for the total energy, forces, transition states, and those for purely electronic parameters like the electronic density, or photo-electron, or electronic spectra. The same features are observed in solid state applications where the accuracy of cohesive energies and lattice parameters does not transfer to the band structure. Such electronic properties do not depend upon the core–core repulsion at all, yet for many of the total energy properties, as we saw for SiO_2, only the core repulsion parameters need to be changed to get agreement with CCSD. This is not surprising. For total energies and forces, we are fitting the difference between two large numbers, which is much easier to fit than the much larger electronic energy, itself. It would be nice to develop a method that fully accounts for whatever the appropriate cancellation of the core–core effects with the electronic effects from the beginning. Only an ability to describe both reliably will pay the dividends of a truly predictive theory.

DFT, MP2, and even higher level methods will continue to progress using local criteria [41], linear scaling, various density fitting tricks [58] and a wealth of other schemes; but regardless, if we can make a transfer Hamiltonian that is already ~4–5 orders of magnitude faster than DFT, retain and transfer the predictive quality of *ab initio* or DFT results for clusters to very large molecules, there will always be a need to describe much larger systems accurately and smaller systems faster. In fact, it might be argued, that if such a procedure can be created that will be able to correctly reproduce high-level *ab initio* results for representative clusters – and fulfill the saturation property we emphasized – the final results might well exceed those from a purely *ab initio* or DFT method for ~1000 atoms. The compromises made to make such large molecule applications possible, even at one geometry, forces restricting the basis sets, or number of grid points, or other assorted elements to acommodate the size of system. In principle, the transfer Hamiltonian would not be similarly compromised. Its compromises lie elsewhere.

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