Reactive interatomic potentials and their geometrical features

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Abstract. We discuss various approaches to modeling the interatomic interactions for molecular dynamics with special focus on the geometrical structural properties. The type of interactions considered are so called reactive force fields, i.e. interactions without predefined bonds and structures. The discussed cases cover the well known Stillinger-Weber, Tersoff-Brenner, EDIP, ReaxFF and ABOP interaction models as well as some additional examples. We discuss also a recently published synthesis of diamond-like structures by isotropic pair potential with multiple minima and use this concepts to propose a sort of classification scheme for interactions with respect to the geometry modeling. In most details we discuss the Tersoff-Brenner potentials and also Stillinger-Weber potential, since these models still appear quite popular in recent research, even though the newer models are more efficient in most respects, except of simplicity. We also propose simple modifications of the basically three-body interactions in order to attempt the simulation of four-body correlation effects. The main motive for this study has been to find how the geometrical features are related to theoretical concepts and whether all possibilities for simplification are exhausted. We conclude that there are large variations in the methods to design the empirical interactions, it does not seem possible to conclude that all possible simple approaches have been considered, since the mentioned recent multiple minima isotropic pair potential method remained undiscovered until quite recently. Though this particular method does not have a direct practical importance, we find its recent discovery as an indication that possible simpler alternatives to the existing models should be explored. This paper also forms a basis for our work with new simple interaction models which is presently submitted for publication.
1. Introduction

From some recent papers a reader might get the impression that the empirical potentials are no longer necessary because the advances in computing will soon allow quantum mechanical calculations of atomic interactions based on, e.g., density functional methods for nearly any type of atomic scale simulations. This work shows, among other things, that the empirical potentials are still used in many applications and will probably remain to be used for studies of some aspects of particle systems for a long time. The project reported here started as a simple investigation of how do the Tersoff-Brenner potentials (Tersoff, [1] [2], [3]; Brenner [4] and second generation [5]) model the geometrical or stereochemical features of the modeled aggregates of atoms. During this work we found details about a number of alternative approaches and the comparisons between the various features lead us to the presented analysis. These results should be useful for researchers starting work on various molecular structures of the type covered by any of the mentioned approaches to atom-atom interactions, as well as for projects aiming at development of improved or combined systems.

The popularity of Tersoff-Brenner and the other so-called bond-order potentials seems to be based on their relative simplicity. The formulae for the potentials contain only elementary functions, a set of parameters is available for many situations, and the development of simple computer codes is quite easy. Additionally, a number of computational implementations are freely available. One aspect which seems also important is that they appear as two-body interactions, where the influence of the other atoms is included in the ”bond order” representation. On the other hand, an analysis of the potentials has not been presented very often. A most complete discussion which we are aware of is in the paper on ”second generation bond order potentials” where Brenner is one of co-authors. This paper is quite long and contains many interesting views.

The purpose of the present paper is to analyze generally these so-called reactive potentials, or perhaps reactive model interactions, many of them associated with the term bond order potentials. We try to compare their features, find out how simple they really are, how well they fulfill the promised function and in particular to prepare ground for possible further work on new alternatives. In spite of their apparent simplicity the work with the potentials is quite convoluted, and the possible simplifications do not appear without a critical analysis. It seems that most of the workers in this field do not find time for such an analysis, since the interest mainly lies in the applications.

We address also the question whether the ’bond order’ approach is really flexible enough to accommodate the ’known chemistry’. The authors of the existing approaches bring many arguments for the positive answer, but it is not easy to see if these are all really valid. In the field of simulations a concept of ”transferability” has been established, which mainly describes the same quality, but puts stress on the performance rather than what one could call usual scientific criteria.

The paper is organized as follows: In the following section we review some example
applications and different requirements put on the potentials in order to provide a certain reference frame. In section 3 we introduce in both historical order and increased complexity order the various potentials (or interaction models). We start with a recent isotropic pair interaction which in spite of isotropy generates the diamond structure. This gives us the possibility to introduce what we call RST-SW axis for classification of the all the interactions discussed. The following part of this section introduces in 3.1 the well known Stillinger-Weber potential [6], followed by Tersoff potential in section 3.2 and six other interaction models. Among the models discussed are interactions known as EDIP, ReaxFF, as well as interactions based on training of artificial neural networks in section 3.7. In section 4.1 we analyze the Tersoff-Brenner potentials and try to bring them into a more general form of a many-body potential. We also address the questions why the potentials are not additive and why the functional form of exponentials is preferred, especially when other forms were used in some earlier works. We also shortly comment on the concept of PES (potential energy surface, or rather hypersurface) which is a starting point of the works outside of the ”bond order” potential approach. In short, the potential as approximation to PES is contrasted to the concept of bond order as starting point. In section 4.2 we investigate where and how the geometrical features are implemented. We also discuss the functional shapes of the potentials.

In section 4.3 we discuss how to possibly add the four-body aspects to the existing models, without major redefinitions, also with respect to the modifications of the cut-off treatment in section 4.5.

2. The various applications of molecular simulation methods

A review of many various approaches and illustrative examples is given in Binder et al, ref. [7]. However, this very nice review by far does not cover all the types of applications which one can find in the exploding research in nanoscale sciences. Also many monographs exist, we refer here as an example to a very extensive book on Molecular modeling by Leach, [8] with more than 700 pages. In this section we will shortly discuss some less usual or even perhaps surprising applications.

Applications of molecular dynamics range from first principles high quality quantal calculations to very simple model potentials of Lennard-Jones or Morse type described in detail in the above mentioned reviews. There are also differences in the treatment of the mechanics itself (e.g. Car-Parrinello [9]), but main focus is on the classical Newton equations derived using various forms of potentials to yield the forces acting on the nuclei. For completeness, one should perhaps mention the Monte-Carlo approaches (review e.g. in [7] or [8]), where the focus is not on the time development, but on - put simply - walking randomly through geometrical configurations and looking for the minima in the potential energy.

The Tersoff-Brenner potentials are mainly applied to silicon systems and to carbon compounds, including hydrocarbons. The two atoms, C and Si belonging both to the group IV and having a very similar structure from the point of atomic physics, have
very different chemical properties. This can mainly be associated with different ability to form $\pi$ bonds, which again from the point of simple molecular physics can be illustrated by the two oxides, $\text{SiO}_2$ and $\text{CO}_2$. It is thus to some degree surprising that the Tersoff-Brenner potentials can be used for both silicon and carbon.

In the so called 'Car Parrinello method' (CPMD) [9] one can be trying to replace the model potentials by quantum chemical results for the electronic energies from density functional theory, usually based on pseudopotentials for the electronic motion. In a very informative tutorial review of molecular dynamics methods [7] the authors remark about the CPMD that the huge advantage is that one is not relying on 'often ad hoc' effective interatomic potentials which lack 'any firm quantum chemical foundation'. This characteristics of the MD-potentials seems appropriate, but it is surprising that the authors use the wording 'quantum chemical foundation', where simply 'chemical foundation' would be definitely more appropriate. It is indeed a fact that the quantum chemical methods are 'more fundamental' than any effective potentials can be, but the ultimate benchmarks are the results of real world chemistry and physics, using whichever are the most appropriate experimental and measurement techniques the various disciplines might provide.

There are many different types of use for the empirical reactive potentials. Some of them are related to the studies of structures of silicon. Silicon has an enormously complicated variety of phases in the condensed state, both crystalline and amorphous. The Stillinger-Weber potential [6] discussed below has been primarily designed for the study of diamond-like Si structure, literature on further studies counts possibly hundreds of papers. It has generally been concluded that the Stillinger-Weber approach is too simple or rather rigid to model the many possible aggregates of Si atoms. Another area are the studies of carbon related structures. One of the most exciting areas are the studies of transition from graphite to diamond, creation of various types of thin films of carbon structures and other carbon nanostructures. Here the literature goes possibly to thousands of various studies. A recent review of the research on carbon nanostructures for advanced composites, [10] reviews also the molecular modeling, with many examples of the use of empirical potentials.

If classified by methods used, there are investigations based on classical deterministic MD, papers using Monte-Carlo methods, comparisons of empirical potentials with the $ab\ initio$ calculations, studies involving processes like irradiation by X-rays resulting in rearrangement of the atoms (modification of bonds), bombardment of surfaces. This short account should be illustrative enough for the observation that there are many aspects which are sought to be understood and that not all of the current uses can be served by the $ab\ initio$ methods. The empirical interaction models will have their use even with increased computational capacity of future hardware. One example is a very recent (2008) study of transformation of graphite to diamond under shock compression [11], where the main method is the Car-Parrinello approach [9], but Tersoff potential studies are conducted to investigate the role of finite size. Thus, even if some aspects are examined in $ab\ initio$ framework, the other aspects might be more
straightforward to simulate in the framework of empirical potentials.

One question which could be addressed also by the empirical potentials is the existence of the so-called cubic and hexagonal versions of the diamond structure. For diamond, these two phases are well documented and known as simply diamond or cubic diamond on one hand, and lonsdaleite, or hexagonal diamond on the other hand. This question has been addressed by DFT studies [32], but to our knowledge not implemented in the framework of empirical potentials. In sections 4.2 and 4.3 we discuss how this can be done.

3. Potentials

In this section we review the most usual reactive potentials, or one should perhaps use the expression ”interatomic interaction models” to cover all of the models. Simple expression ”potentials” is really appropriate only for the earliest models. This review tries to cover most of the different types of models, but it simply cannot be complete since there are many variations in the vast existing literature. One aspect to look for is to which degree the method attempts to obtain the empirical potential as an approximation to PES (potential energy surface). This aim is explicitly stated in some formulations. In other approaches, this aim remains perhaps implicitly present but explicitly other modeling aims are expressed. This refers in particular to the explicit reference to ”bond order” in most of the newer approaches discussed here.

We start the discussion by referring to a recent work of Rechtsman, Stillinger and Torquato [12] discussing what they called ”synthetic diamond and wurtzite structures” which are self-assembled using only isotropic pair potentials. We shall refer to this work as RST.

The two model potentials given in the paper appear as somewhat weighted negative functions of the radial distribution function (RDF) for the two structures. It means there is a general background potential with narrow minima at the positions where the RDF has peaks. Clearly, the first local minimum corresponding to the nearest neighbor must be rather shallow and above all the other minima, otherwise only a closed packed structure will be the stable one. Unfortunately, the authors do not describe how they have arrived to the particular parameterizations, i.e. the extra weights, but they describe in sufficient detail how they obtain the positions of the minima, i.e. the distances between the next neighbor points of the lattices.

These potentials are important for our discussion, because here no angular dependence of the forces between atoms is included, and the potentials are only two-body potentials. This means that this interaction model does not carry any explicit geometrical features. All geometry is provided by the structure of the Euclidean space itself. This will give us a possibility to classify the other interactions discussed according to the degree of explicit geometrical features.

When reviewing the potentials, we meet again and again the concept of bond order, and thus we should have a more or less precise definition of this concept. That is not
Reactive potentials and geometry

Figure 1. Schematic reproduction of the synthetic diamond lattice potential. Full line traces the shape of the potential, curved dashed line the background potential, and the lower dotted line the scaled negative of smeared RDF, which is superimposed on the background potential. Note, this is only schematic. It is not a description of how the authors constructed the potential.

easy, since these words are used with at least two different meanings. IUPAC definition of bond order can be summarized as follows: considering the region - it is measure of electron population in the region between atoms A and B which is moved from the atomic regions of the two centers. In Mulliken’s formulation this is expressed with the help of the electron density matrix. In valence bond theory the bond order is related to the formal bond orders obtained from the Lewis structure. The Mulliken’s formulation is related in some way to the electron density, and will be changing when the configuration is changed. The valence bond alternative is related to stable configurations and does not have any clear relation to the distance between the two atomic centers. The exponential relation between the bond strength and bond length has been studied by Pauling, also there for stable configurations. The exponential form of this dependence has been suggested and in many studies the simple rule has been confirmed as approximately valid. The relation of bond strength and bond order are rather unclear, as this reference shows.

3.1. Stillinger Weber potential

The Stillinger and Weber potential is the simplest model of non-isotropic interatomic attraction, including three body potentials. It is realized with the help of an isotropic (only distance dependent) two body terms with the addition of three-body terms which depend on the angles between two bonds in each of the triplets. This interaction model includes thus the correlation between any three neighboring atoms and assures that the preferred bond angle is the so called tetrahedral angle \( \tau \) given by \( \cos \tau = -1/3 \). No further considerations of the geometrical relations to other atoms are necessary, it is
enough to require the bond angle to be close to 110 degrees. This requirement implicitly defines the 3 dimensional geometry, since in a plane we can not attach two more atoms to a central atom in an existing triplet and keep all angles close to 110 degrees. Thus only four neighboring atoms (three bonded to a fourth in the center) can be in one plane with angles 120 degrees, the fifth atom (or the fourth closest neighbor of the central atom) must be out of plane, which results in the rearrangement of the five neighbors into the tetrahedral structure.

The situation is thus similar to the one discussed in the synthetic pair potential case, where however absolutely no geometry was included explicitly. In Stillinger-Weber case only one element of the geometry is included, a preferred bond angle, all the rest is left to the properties of the Euclidean space. We will classify the remaining potentials by their position along the RST-SW axis, where RST is zero and SW is one.

Stillinger and Weber defined their potential as

\[
\Phi(r_1, r_2, r_3, ..., r_N) = \sum_{i<j} v_2(r_{ij}) + \sum_{i<j<k} v_3(r_{ij}, r_{jk}) + ....
\]

and introduced energy and length units, \( \varepsilon \) and \( \sigma \),

\[
v_2(r_{ij}) = \varepsilon f_2(r_{ij}/\sigma) \\
v_3(r_{ij}, r_{jk}) = \varepsilon f_3(r_{ij}/\sigma, r_{jk}/\sigma)
\]

\[
f_2(r) = \begin{cases} 
A(B(r^{-p} - r^{-q})) \exp \left[(r-a)^{-1}\right], & r < a \\
0, & r \geq a
\end{cases}
\]

\[
f_3(r_{ij}, r_{jk}, r_{ki}) = h(r_{ij}, r_{ik}, \theta_{ijk}) + h(r_{ji}, r_{kj}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})
\]

where \( \theta_{ijk} \) is the angle between \( r_{ji} \) and \( r_{ki} \), at the vertex \( i \). The functions \( h \) have two parameters, \( (\lambda, \gamma) > 0 \), which is nonzero only if both \( r_{ij} < a \) and \( r_{ik} < a \)

\[
h(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda \exp \left[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}\right] \left(\cos \theta_{ijk} + \frac{1}{3}\right)^2
\]

and identically equal to zero outside of these two conditions.

They made a limited search, their parameters:

\[
A = 7.049556277, \quad B = 0.6022245584 \\
p = 4, \quad q = 0, \quad a = 1.80 \\
\lambda = 21.0, \quad \gamma = 1.20,
\]

where the units are Ångström and electronvolt. The SW-potentials are mostly considered as only of historical interest, However, we can refer to a very recent (2009) study [13], where the authors modified and used SW potentials for reactive ion etching simulations.
3.2. Tersoff’s potential

Tersoff started by defining a two-body interaction, building on the concept of bond order, mentioned above. The form of the potential is rather complicated and it will thus be interesting to classify this interaction along the RST-SW axis.

\[ E = \frac{1}{2} \sum_{i,j \neq i} V_{ij}, \]  
(6)

\[ V_{ij} = f_c(r_{ij})[a_{ij} \exp(-\lambda_1 r_{ij}) - b_{ij} \exp(-\lambda_2 r_{ij})] \]  
(7)

where \( f_c(r) \) is a cut-off function defined below. Here the first term is referred to as repulsion, the second as attraction. The form for \( b_{ij} \) is:

\[ b_{ij} = \left[ 1 + \left( \beta \zeta_{ij} \right)^n \right]^{-\frac{1}{2n}}, \]  
(8)

\[ \zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3(r_{ij} - r_{ik})^3], \]  
(9)

\[ g(\theta) = 1 + \left( \frac{c}{d} \right)^2 - \frac{c^2}{d^2 + [h - \cos \theta]^2} \]

note that \( b_{ij} \neq b_{ji} \) - asymmetric formulation. \( a_{ij} \) proposed form is:

\[ a_{ij} = \left[ 1 + \left( \alpha \eta_{ij} \right)^n \right]^{-\frac{1}{2n}}, \]  
(10)

\[ \eta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \exp[\lambda_3^3(r_{ij} - r_{ik})^3] \]

If \( \alpha \) is sufficiently small then \( a_{ij} \approx 1 \); Tersoff set \( \alpha \) to zero so that \( a_{ij} = 1 \). The cut-off function \( f_c(r) \) used by all Tersoff followers:

\[ f_c(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi}{2} \left( \frac{r - R}{D} \right) \right], & R - D < r < R + D \\ 0, & r > R + D \end{cases} \]  
(11)

The complicated functional dependence of the Tersoff-Brenner potentials can be contrasted to that of Stillinger-Weber potential which is explicitly of three-body character only, given by the simple form containing separately two and three body terms

\[ V = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_{ijk} g(r_{ij}) g(r_{ik}) \left( \cos \theta_{ijk} + \frac{1}{3} \right)^2 \]  
(12)

where \( \theta_{ijk} \) is the angle between \( ij \) and \( ik \) bonds, \( g(r) \) is a decaying 'cut-off' function.
3.3. REBO - Second Generation Brenner Potentials

Second Generation Reactive Bond Order Potential (REBO) has been introduced by a group of authors including D. Brenner in [5]. Much work has been done since the first 1990 paper of D. Brenner [4]. The main features of our interest here, however, remain mainly unchanged. The interaction model is made more complex and extensive fitting is performed, so that the resulting REBO model interaction is applicable to mixtures of atoms. The structure outlined for the Tersoff model in section 3.2 is mainly applicable also here.

3.4. EDIP - Environment dependent interaction potential

The environment dependent interaction potentials (EDIP) are first more complex models of interatomic interactions. The angular three body contributions and the two-body terms depend on the configuration of the atoms, i.e. on the number of neighbors, also known as the coordination number. This is the characterization of the environment. The angular parts are of the Stillinger and Weber type. For silicon compounds they were introduced by Bazant and coworkers in [17] and [18], some years later extended to carbon by Marks [19] and applied to diamond studies in [20] by the same author. With the help of switching functions depending on the coordination number extra terms, dihedral rotation penalties and $\pi$-repulsion are added to the features of original EDIP for silicon. Due to the addition of $\pi$-orbital features, the Stillinger Weber functionality is considerably extended, and since there is one more geometrical feature involved, we assign to EDIP the value of 2 on the SRT-SW axis.

3.5. Long Range Carbon Bond Order Potential - LCBOP

Quite recently (around 2004) a new version of interaction of Brenner bond-order type has been introduced in references [28], [29] and also reported in [30]. The authors call it Long range Carbon Bond Order Potential, i.e. LCBOP. This potential is thus the most recent of all the discussed ones. It demonstrates that relatively simple model interactions can successfully model broad range of features when new elements of design are included. In some features this model interaction is simpler than Tersoff-Brenner type (the angular functions), while it adds complexity to the coordination number dependence and the long range part. Perhaps unfortunately, it still remains in family of interactions where the three body angular effects (bond angles) are entered via pair interaction (bond order) mechanism.

3.6. General ReaxFF approach

This interaction model was named ReaxFF, and has been introduced as “Reactive Force Field for Hydrocarbons” in 2001 [31]. Also ReaxFF is using the bond order concept, following Tersoff’s terminology, but the models contain much more freedom, i.e. many more parameters. The structure of the model is much more rich than any of the other
"potential" models discussed here. It can nearly be said that it contains elements from all the other models discussed. In addition to pair interaction there are penalty functions for non-matching coordination number and bond angles. The functional forms appear mostly as additive terms, generally they do not appear in the convoluted functional forms typical for "bond order potentials" of Tersoff-Brenner type.

The ReaxFF models depend on a very large number of parameters and they provide a very realistic model of the chemical knowledge. The parameters are obtained in a process which is quite appropriately denoted by use of "training set", in analogy with the language used in non-linear optimization of the neural networks type. The structure of the models is rather complicated, but it is well described in the original papers. From the original purpose as model for hydrocarbons it has been extended to describe gradually more and more atomic combinations, at present ReaxFF covers large portions of the periodic table.

Our classification on the RST-SW axis this method should be assigned at least number 4, since in addition to several types of angular correlations also additional electrostatic effects are included.

This method should certainly be considered as an alternative to the simplest approaches above. On the other hand, the model is very complex (being very accurate), and thus it might be too complicated for some applications which would require simplicity. In any case, the data collected and used in the "training" of this simulator can be very useful for design of simpler special purpose empirical potentials in the future.

3.7. Artificial neural networks based model interactions

There have also been proposals to replace the model interaction by potential functions provided by a suitable artificial neural network (ANN). In 1999 S. Hobday et al [34] investigated the feasibility of such approach by training a network to mimic the Brenner potential, i.e. the energy surface was not evaluated by the Brenner formula, but returned by the ANN, or in other words the ANN was trained on configurations where the energy has been given by the Brenner formula. The aim of the experiment was to test the method which in future applications would use not a simple and known potential, but as broad as possible physical and chemical data to train the ANN.

In a recent study, Bholoa et al [35] the ANN which gives energy surface for given local atomic positions is trained on thousands of data points for a wide range of silicon systems obtained by the tight-binding (TB) calculations. The network had 9 nodes in the input layers, two or three hidden layers with about 11 hidden nodes in each layer and the energy value as the output. The authors report a very good performance of such ANN which replaces the potential form.

The idea of the method is very close to the prescription to use as much as possible of the accumulated knowledge to design the model interactions. Here the authors attempted to use the known advantage of ANNs to represent knowledge which does not have a simple logical structure, which makes these methods suitable for character
recognition, speech recognition and many areas of nonlinear optimization.

In practical calculations this method has proved to be relatively slow when competing with the direct Brenner formula evaluation. It would however probably be much faster than any ab initio method, while it could be trained on very thorough quantal calculations. After all, in MD context only the resulting energy landscape is of interest, not the quantal mechanisms themselves. The disadvantage of this approach is similar to the ReaxFF: a very high fidelity of the model is in principle possible, but the actual physical features of the model are in this case completely hidden. (In the ReaxFF there are so many features that their mutual roles are effectively hidden).

3.8. Simulations based on First Principles

The expression "first principles" is often used to classify an approach as the one based on only the most fundamental assumptions, and in our connection it would often refer to inclusion of methods of quantum chemistry into the procedure of modeling interatomic forces and formation of the chemical bonds (though many could object to the latter formulation, the meaning would be probably accepted). If taken literally, a true "first principles" approach along these lines would be built on the following Hamiltonian which should be solved in the framework of quantum mechanics. For a moment we keep the kinetic energies denoted by $T(r)$, which can be replaced by their classical as well as quantum representations

$$T(r_\alpha) \longrightarrow \frac{1}{2} m_\alpha \dot{r}_\alpha^2$$

$$T(r_\alpha) \longrightarrow -\frac{\hbar^2}{2m_\alpha} \nabla^2 r_\alpha$$

schematically

$$\sum_{\text{nuclei } i} T(R_i) + \sum_{\text{nuclei } i > j} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{\text{electr } \alpha} T(r_\alpha) - \sum_{\text{nuclei } i} \sum_{\text{electr } \alpha} \frac{Z_i}{|\vec{R}_i - \vec{r}_\alpha|} + \sum_{\text{electr } \alpha > \beta} \frac{1}{|\vec{r}_\beta - \vec{r}_\alpha|}$$

The summations over electrons can be grouped into the atoms and Born-Oppenheimer type approximations can then be used much like in the so called semiclassical collision theory for atom-atom or molecular collisions. Further, a series of well defined and controlled approximations could be carried out further to arrive at different simulation methods (a useful review has been given by Marx and Hutter [36]).

Following Kohn’s Nobel lecture [15], one can ask if such ambitions are in fact fruitful. We know that chemistry does not violate any physical first principles, but we also know that many situations which chemistry describes may become extremely dependent on from the point of physics more or less surprising accidental dependences on geometry, accidental quantal energy degeneracies and many other effects which are not possible to be seen from the formula above. Thus, one should always have in mind that
quantum chemistry can never fully replace the laboratory and the ever richer toolboxes of physical chemistry.

The purpose of this statement is to realize that a really fruitful future of the empirical potentials, including an obvious advantage over the 'more fundamental' methods is to build empirical interactions which are based on all accessible relevant chemical and physical data instead of on requirements of simple functional form or derivability by complex approximations from a 'more fundamental' formulation.

In quantum chemistry, the above Hamiltonian with various approximations is solved using various types of selfconsistent field approaches, recently mostly based on density functional theory (DFT), earlier on Hartree-Fock (HF) approaches. Historically, a very successful approaches have been based on linear combinations of atomic orbitals, LCAO. In solid state physics the LCAO approaches have been adapted to the so called tight binding approximation (TB), where the geometry could enter in a very simplified form, which was very useful both for qualitative understanding as well as numerical evaluation of the electron energy band structure (e.g. the well known work of Slater and Koster [21]).

In fact, the "first principles" methods can be built on much less fundamental principles, approximative methods like the tight binding method or density functional theory are used. In the literature both the DFT methods and the TB methods are referred to as \textit{ab initio} methods.

3.9. \textit{ABOP} - Analytic Bond Order Potentials

The Analytic Bond Order Potentials (ABOP) are reviewed in ref. [24]. This approach follows the work of Pettifor and Oleinik [25], who attempt to go beyond the Tersoff’s assumptions, and it can be described to be in fact based on the tight binding approximation, [21] [22] [23]. The tight binding molecular dynamics is a large field with lots of locally adopted concepts which might sometimes make it difficult to follow for workers outside of the field. The geometrical features are included in a really fundamental manner, building on the angular dependence of the exchange or hopping matrix elements. However, the formalism of the derived model interactions is rather complex and will not be reviewed here. The review in ref. [24] can be consulted for details.

The ABOP thus attempts to include consistently an approximation to the quantum chemistry and on our RST-SW axis it should be given at least index 3, since in principle all the aspects of the geometry following from quantum theory are included. They should certainly be considered as an alternative to the simplest approaches above, but on the other hand they might be too complicated for some applications.
4. Tersoff and Brenner Potentials

As discussed above, these potentials were originally suggested and explored by Tersoff and later modified and extended by D. Brenner and coworkers with a wide selection of applications. To some small degree the functional forms but mainly the parameters were modified to suit many different systems. There are hundreds of works using one or other form of these potentials, as well as many further modifications and adjustments. A full review of all these attempts is virtually impossible to be carried out in a reasonable format, however it might be illustrative to select some examples. One of the examples can be the use of Brenner potential for simulations of the self-assembly of fullerenes (1998), carried out by Yamaguchi and Maruyama[16].

We will however, try to analyze these potentials, which gave the name to the whole method, as "bond-order potentials". As seen from the above section, not all of the empirical potentials are necessarily connected with this particular interpretation of the bond order concept.

4.1. Many body character of Tersoff interaction

In this section we attempt rewriting the Tersoff potential in a general form, as a many-body potential. Why are they not additive as SW or ReaxFF? And why is the functional form always an exponentials? The many-body interaction in Tersoff approach is in fact written in the following general form

\[
V(r_1, r_2, \ldots, r_N) = \frac{1}{2} \sum_{i \neq j} F_{ij} \left( \sum_{k \neq i, j} G(r_i, r_j, r_k) \right)
\]

One can imagine that this form is a result of a certain summation of this type of series:

\[
V(r_1, r_2, \ldots, r_N) = \sum_{i,j:i<j}^\text{(pairs)} P_{ij}(r_i, r_j) + \sum_{i,j,k}^\text{(triplets)} T_{ijk}(r_i, r_j, r_k) + \sum_{i,j,k,m}^\text{(quadruplets)} Q_{ijkl}(r_i, r_j, r_k, r_m) + \ldots
\]

in the sense described by Stillinger and Weber. Only special types of the latter general expansion when summed would result into the former type of expression. It is thus a model assumption, based on the idea of 'bond order', i.e. the variable strength of the interaction, which in Pauling's empirical formula [26] is related to the length of the bond. In his work on empirical chemical pseudopotentials for metallic bonding Abell [27] further generalized (somewhat arbitrarily) this dependence to reflect also the environment of the two bonded atoms.

In the ABOP formulation, the mentioned shape is attempted to be derived from a summation, using a certain type of Green's function formulation. The ABOP potentials are based on TBMD applications, modeling the diagonalization of sparse matrices. This is a very appealing approach, since it provides to some degree a sound theoretical basis for the whole bond-order approach, as discussed in the section 3.9.
4.2. The geometry treatment in the Tersoff Potentials

The geometry treatment is in fact of the same type as that of Stillinger - Weber, i.e. simply the preferred angle is contained in the function $g(\theta_{ijk})$, where $\theta_{ijk}$ is the angle between the lines connecting the three atoms

$$g(\theta) = 1 + \left(\frac{c}{d}\right)^2 - \frac{c^2}{d^2 + [h - \cos \theta]^2}$$

The value of $h = -0.598$ given in Tersoff’s paper selects the bond angle 126.7°, while in Brenner’s case this is sometimes replaced by 180° (this is probably only an omission in the paper, listing only one value). Clearly, only one angle can be included. Which

![Diagram of \(i\), \(j\), and \(k\) atoms with \(\theta_{ijk}\) angle](image)

**Figure 2.** This figure attempts to illustrate the Tersoff basic method. The interaction appears as a two body potential, but the strength parameters for the pair i-th and j-th atom are calculated using the angle of (all) k-th atom(s). The dependence on the angle between the bonding lines enters in a complicated way into the evaluation of the attractive part of the interaction between i-th and j-th atom (cf. eq. 8)

then poses a question - how can Tersoff-Brenner potentials model both graphenes and diamonds. The answer is that it is not the potential itself, but the interplay of the

![Diamond (a) and hexagonal lonsdaleite (b)](image)

**Figure 3.** Diamond (a) and hexagonal lonsdaleite (b)

potential and the properties of the space. It is possible to change a little bit the parameters, but the same potential only allows one angle.

The bond order strategy can be characterized as follows: the effect of the angular correlation is expressed by influencing the bond strength (order) of the bonds formed
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by other pairs. The three body correlation characterized naturally by the angle between the bonds is in BOP instead taken into account by expressing the strength of both neighbouring bonds as rather complex functions of the angle between the bonds. Adjusting these functions and their parameters to chemical data and results of quantum chemical calculations is thus quite complicated procedure. This is in contrast to the simple form of angular dependence in the Stillinger and Weber which is expressed as an additive term.

4.3. Tersoff-Brenner potential and four particle geometry

A given carbon atom both in the Diamond and Lonsdaleite structures has up the second neighbors completely identical neighborhoods, the differences appear first by the third neighbors as can be understood from figure. The interaction with the nearest neighbors can be sufficiently well represented by a three-body interaction of as simple type as the Stillinger-Weber type. (Tersoff-Brenner potentials contain in principle more complex correlations). To differentiate between the two different 4-atom conformations (aliphatic type and ”boat chains” - see again the figure in the two discussed structures, a 4-body correlation must be made effective in the interaction model.

Due to the implicit sum over all triplets in the bond strength of the Tersoff-Brenner potentials, one would expect the possibility to have a 4-body correlation. However, with the cut-off function used in the standard formulation, the mutual influence is limited to the nearest neighbors, the standard cut-off prevents any higher than 3-body correlation. This is not inherent limitation of the model, it is simply the choice of the cut-off parameter.

If the repulsion part (cf. equation) would be allowed to act over a longer range (using a different cut off for each of the two terms), one could in principle model a four body correlation (using only 3-body interactions) without any other modifications of the Tersoff-Brenner model. One should realize that different cut-off could lead to a little positive energy (repulsive) region, appearing as a little barrier in the two atom case.

Without such type of modification, both Tersoff-Brenner and Stillinger-Weber interactions lead to a situation where both diamond and lonsdaleite are energetically completely equivalent.

4.4. Investigation methods

We have developed several simple techniques to study the angular aspects. For this purpose we have written small tools for several mathematical systems. In order to be able to perform quickly evaluation of forces from potentials, we have developed a code in Mathematica (to allow even the inspection of the analytic form of forces), as well as in Maple. However, the advantages of the analytic form are shadowed by the complexity and length of the expressions, so the usefulness of this approach is limited in this context (some examples can be found in the thesis). More recently we have used MATLAB, which is much more suitable for numerical inspection. In this
connection we have used the ability to perform mathematical operations on complicated structured objects in one single statement using ordinary mathematical notation. Thus an evaluation of potentials or forces which would in other computer languages require a whole special computer program can be not only evaluated, but also visualized in a couple of lines which are directly interpreted. The MATLAB work is available as preprint [41] and submitted for publication. (Open source systems GNU-Octave and SCILAB can have very close syntax and functionality so that some of our shorter scripts for MATLAB can also be applied using these two free systems.)

The functional dependence of the empirical potentials discussed is not really given by any very thorough tests. A convenient form has been chosen at a certain point and the information is carried by the parameters. The question about how optimal the functional shapes really are has not been raised.

4.5. Form and cut-off of Tersoff potential

For Tersoff-Brenner potentials, most of the active forces are in fact provided by the cut-off function, as the figure 4 shows. Stillinger-Weber use a different, simpler function, which could easily be used also by Tersoff-class of potentials. The cut-off function used by all Tersoff-Brenner applications is the cosine-type cut-off formula eq. 11 which does not have a smooth derivative. In all our work we have replaced it by the Fermi function (exp((r – r₀)/d) + 1)^{-1} which is smooth everywhere and the parameter d can be easily adjusted. Figure 5 shows the comparison of the two cut-off treatments.

Figure 4. The potential and force with Tersoff-Brenner and Fermi cut-off functions; (a) Potential shape without any cut-off in solid red, with Tersoff-Brenner cut-off in dashed black, with Fermi cut-off in solid blue; (b) The corresponding forces with the same notation as in (a)
4.6. Extending Stillinger-Weber approach by four-body correlations.

The four-body correlation energy, usually referred to as dihedral angle potential, could be added to the Stillinger-Weber model by introducing a four-body term, formally completely analogous to the already present three-body term. However, as discussed in the section 4.3 above, one could also attempt to add an effective four-body correlation mechanism by only choosing suitable modifications of the existing model. We want to concentrate on the question which can be formulated as that of difference between diamond and lonsdaleite, or in much more complicated way as the dihedral angle dependence. With only three-body correlations taken into account, Stillinger-Weber potentials will lead with more or less equal probability to both cubic and hexagonal lattice formation. On the other hand, a realistic potential should be able to distinguish between these arrangements in plane shown in fig. 3. As discussed earlier in Sec. 4.3, Tersoff-type potentials could do that in principle with a modified cut-off treatment. The same effective four-body effect due to a modified two-body interaction can also be extended to the Stillinger-Weber model without introducing a new explicit 4-body term. This can be done by modifying the functions defining the potential shapes defined by equations 3 and 5. The schematic representation of this type of potential is given in figure 6. It shows the usual shape of Tersoff and SW potentials, but also with added a small repulsion region close to the lonsdaleite third neighbor distance. The physical origin of this model term is electron-electron repulsion not accounted for by the independent electron picture implicit in the discussed models. With so modified basic two-body interactions lonsdaleite becomes energetically less favorable than diamond, which is a desirable result, both from observation and from calculations 82, 83.

It is interesting to note that a similar situation is encountered in the hydrocarbons, the alkanes. The diamond-like arrangement is also there energetically preferred. The isomers which have the lonsdaleite analogue structure have a higher energy denoted as...
so called bond strain. In this case the decreased binding is ascribed to the electron-electron repulsion between electron bonding pairs present on any two hydrogens in the boat configuration, fig. 3b.

5. Conclusion

We have discussed the various approaches to reactive model interactions found in literature. We have illustrated how varied these approaches in fact are in several important aspects. We have classified qualitatively the interactions by a position on the RST-SW axis introduced in section 3.1 according to the attempted simulation of the geometrical features.

The recent LCBOP discussed in subsection 3.5 shows that new ideas may still contribute to a usability of relatively simple models. Though the computing progress makes the so called *ab initio* methods increasingly more feasible, simple model interactions might still be very useful for certain types of studies. This is also supported by our discussion of possible inclusion of four-body or dihedral angle effects in the basically three-body models.

Hybrid methods, combining e.g. DFT parts which could provide re-defined parameters in well designed simple model interactions of generalized EDIP-type might become elements of increasing importance as new groups of researchers will use MD-based approaches to address possibly new questions about interest in material sciences and nanotechnological applications.

We conclude that there are large variations in the methods to design the empirical
interactions, it does not seem possible to assume that all possible simple approaches have been considered, since the mentioned recent multiple minima isotropic pair potential method remained undiscovered until quite recently. Though this particular method does not have a direct practical importance, we find its recent discovery as an indication that possible simpler alternatives to the existing models should be explored. This paper also forms a basis for our work with new simple interaction models which is presently submitted for publication.

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