Chapter 7

Conclusion

> Of course, every new potential is claimed by its originators to be superior, i.e., more accurate and/or more transferable than its predecessors. While these claims are often valid to some extent, such improvements are almost always achieved by sacrificing other properties. Also, very often it is not truly clear what causes the better description. Is it due simply to a more flexible functional form and/or fitting strategy or does the new potential really give a better description of covalent bonding?
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> – H. Balamane, T. Halicioglu and W. A. Tiller [19]

Let us objectively discuss our successes and failures and then look forward to the future of EDIP and empirical potentials for covalent solids, in general. Throughout this thesis we have answered many of our motivating questions affirmatively. By reviving and improving several analytic techniques from the literature of solid state physics, we have established various facts concerning the functional form of interatomic forces in the prototypical case of Si directly from *ab initio* calculations, which have proven useful in designing a transferable fitted potential for silicon bulk phases and crystal defects.

Through elastic constant analysis we have studied forces mediated by sp^2 and sp^3 hybrid bonds in covalent structures. In the case of the Harrison model for diamond elasticity, we have demonstrated that a simple, underdetermined functional form can fit a nontrivial manifold on the Born-Oppenheimer energy surface almost perfectly, as evidenced by the elastic constant relation, $4C_{11} + 5C_{12} = 9C_{44}^o$, which is satisfied by experimental and *ab initio* data for Si. We interpret this success as validation of the Rigid Hybrid Approximation for *any* elastic deformation without internal relaxation. For shear strains with relaxation, measured by a nonzero Chelikowsky dangling bond vector, the Harrison model fails because it does not describe rehybridization. We have also confirmed that second neighbor forces in the diamond lattice are very weak, and in the case of a three-constant model have demonstrated that adding a degree of freedom does not guarantee a better fit if the functional form is wrong. Interesting comparisons between different hybrid covalent bonds have also been made by analyzing a Harrison-like model for the elastic constants of a hexagonal plane. Our *ab initio* calculations for Si reveal that sp^2 hybrids have a greater radial force constant but a weaker angular force constant than sp^3 hybrids, an important and counterintuitive result.

In order to explore global trends in bonding across bulk structures, we have performed the first meaningful inversions of cohesive energy curves for a covalent solid. This is accomplished by understanding and solving problems with long-range forces and deriving formulae for many-body interactions. In response to one of our motivating questions, it is indeed possible to derive competitive many-body potentials directly from *ab initio* data without any adjustable parameters. By looking at different bulk phases, we have also exposed environment dependence, showing that the bond order form of the pair interaction is in excellent agreement with theory.

Aside from gaining physical insight through inversion, we have also developed some new mathematics. With our many-body formulae in Chapter 4 and Appendix B, several classes of *nonlinear* inverse problems are solved. The central idea of recursion also finds interesting applications in number theory related to the Möbius Inversion Formula, as described in Appendix C.

On a more practical note, building upon this work we have proposed a functional form for interatomic forces in covalent solids with only 13 fitting parameters, called the Environment-Dependent Interatomic Potential. It blends the desirable features of the Tersoff and SW models we have identified theoretically and includes a new environment-dependent angular function, which adapts the angular stiffness and favored angle to model rehybridization and metalization. An important point is that force evaluation with EDIP is as fast as with much simpler models. A fitted EDIP for bulk defects in Si is remarkably realistic for diamond elasticity and a wide range of defect structures not in the fitting database, including generalized stacking faults and reconstructed partial dislocation cores. The liquid is rather well described, aside from the unphysical splitting of the first neighbor peak of $g(r)$, but the amorphous phase is not correctly modeled by the current version. However, we have identified the sources of these problems and have shown how they can be corrected. With some additional work, it is likely that an EDIP for silicon will provide a superior description of the important bulk phases and defects.

Although we are surely guilty of overstating our successes to some degree, we have made a sincere effort to address Balamane's criticisms quoted above. Our testing has been much more extensive than any other potential prior to publication. In fact, had we stopped testing before looking at disordered phases, we might have thought we had stumbled upon *the* potential for bulk Si from the defect results. It is our goal to thoroughly understand the behavior of our potential, so future researchers can use it with confidence, safely warned about its limitations.

We have also taken unprecedented measures to help us interpret our successes and avoid the ambiguity of blind fitting schemes. In spite of its sophistication, EDIP has hardly any more degrees of freedom than the simplest models, so its successes cannot be due to increased flexibility. Our fitting strategy has also been kept fairly simple, with clear focus on a particular class of environment (bulk crystal defects) that is within our theoretically predicted range of validity. In contrast, other potentials are repeatedly extended to situations where there is no reason to expect success by simply adjusting arbitrary fitting parameters. As far as interpretation in terms of chemical bonding goes, we have demonstrated agreement with inversions of *ab initio* data in several ways, and in those cases success is not merely a matter of luck in fitting. In the majority of cases, however, we must admit that, aside from fitting and testing, we cannot carefully validate many aspects of the EDIP functional form, which surely are inadequate for complete transferability. Nevertheless, we are holding our work to high standards of theoretical and practical validation, because our overall aim in working with the one of the most difficult and extensively studied materials is to understand the general limitations of empirical interatomic potentials.

So, how will we know when to stop working on Si? That is a difficult question, but the answer must surely be, not yet. At this point, many researchers have given up on improving the description of Si, and have moved on to other covalent materials (like Ge, C, S, F, SiF, SiO_2, GeSe, SiN, ...) where less work has been done and the standards of accuracy are much lower. It is certainly important to study these materials, but given the difficulty in describing Si under close scrutiny, it is hard to believe that poorly tested potentials for less well understood materials can be trusted enough to generate realistic simulations. Still, questionable physical validity has not stopped the growing tide of large-scale atomistic simulations, fueled by growing excitement over advances in high performance computation.

In going to new materials that are less well understood, the methods developed in this thesis should be quite useful. For example, the environment dependence of the bond order could be checked for related covalent elemental solids and alloys, and our elastic constant relations could be used to compare angular forces and bond strengths for different hybrid bonds. These properties should be qualitatively similar to Si, but other materials will have important quantitative differences leading to different structural preferences. The EDIP functional form, since it contains environment dependence for metallic bonding and different covalent hybridizations, may provide a unified way to describe all covalent materials. It may be possible to use inversion and elastic constant results to simply rescale the parameters of the Si version of EDIP for other materials to obtain reasonable potentials. If this works, we can claim we have truly learned some general features of bonding in covalent solids.

Even if the dream of quantitatively accurate atomistic simulations with empirical potentials is never realized, there will always be a crucial role for potentials to play in materials science. Compared with accurate quantum-mechanical treatments, empirical potentials provide a means to explore the qualitative effect of going to larger system sizes or longer times. This capability is necessary, for example, to evaluate entropic contributions to free energies, so that predictions of *ab initio* energy calculations of atomistic mechanisms can be extended to finite temperatures. Another important use of empirical potentials is to quickly probe phase space looking for a small set of candidate atomic mechanisms to be studied quantitatively with *ab initio* methods. In other cases, where quantitative comparison with experiment is not needed, the essential physics of a process may be contained in simple models (*e.g.* phase transitions of the hard sphere model in statistical mechanics), so for certain general theories of materials phenomena, empirical potentials may be sufficient for qualitative understanding.

Beyond these practical uses, empirical potentials still have the power to dictate our conceptual understanding of chemical bonding. The concepts of pair bonds and angular forces developed through the models of Born, Harrison and Stillinger-Weber define the way we think about covalent materials. The language by which we understand the results of *ab initio* calculations is influenced by these artificial but useful theoretical constructs: a tendency to have as many nearest neighbors as possible at a preferred distance (and thus maximize the number of unstrained bonds) is countered by an aversion to inappropriate angles. The balance between these competing effects helps us understand atomic relaxations and motion. The Tersoff family of potentials introduces the next crucial concept, that the strength and length of a bond depends on its environment, weakening and lengthening as coordination is increased. The main conceptual contribution of EDIP is the idea that angular forces also depend on the environment, weakening with increasing coordination and shifting the preferred angle depending on the number of neighbors. Environment dependence is the key to understand bonding preferences in defect structures and disordered phases, where different coordinations can arise. It also gives a unified view of competing covalent phases, like diamond and graphite in the case of carbon. The next step will be to understand what kind of environment dependence is needed for surfaces and small clusters, which is beyond the scope of this thesis. An important part of this task would be an analysis of π-bonding, which we have safely ignored in this work. At least in the prerequisite case of bulk material, we have contributed to the theoretical understanding of interatomic forces in covalent solids.