Chapter 3

Elastic Constant Relations

In 1914 I had published a paper on diamond. I assumed two kinds of forces, a radial force between two nearest neighbours and an angular force involving three neighbours. Therefore, I had two independent atomic constants. But the (cubic) crystal has three elastic constants; therefore the theory provided one relation, namely $4C_{11}(C_{11} - C_{44})/(C_{11} + C_{12})^2 = 1$. At the time no measurements of the elastic constants of diamond existed. I had to wait 31 years. Then, in 1945 in Edinburgh, I learned about new supersonic methods to measure elastic constants. Remembering the old formula, I wrote to my friend Franz Simon...and suggested to him to put one of his pupils on to this problem. Before I had finished this letter, the postman brought me my mail which included a paper by the Indian physicist Bhagavantam. It contained just these three measurements. Inserting his figures into the formula I obtained instead of 1 on the right hand side, the value 1.1 – quite a satisfactory confirmation.... This paper started off a series of investigations...establishing relations between macroscopic constants by making simple, natural approximations about the lattice forces.

– Max Born [70]

A useful theoretical approach to guide the development of potentials is to predict elastic properties implied by generic functional forms and compare with experimental or *ab initio* data. Recently, this method has been pursued by only a few authors [71, 72, 21], but apparently they did not search for elastic constant elastic constant relations implied by simple functional forms, which is our approach. This tool for understanding interatomic forces dates back to the 19th century, when St. Venant showed that the assumption of central pairwise forces supported by Cauchy and Poisson implies a reduction in the number of independent elastic constants from 21 to 15 [73]. The corresponding six dependencies, given by the single equation $C_{12} = C_{44}$ if atoms are at centers of cubic symmetry, are commonly called the Cauchy relations [73, 74]. They provide a simple test for selecting which materials can be described by a pair potential [11, 75]. Once it was realized that the Cauchy relations are not satisfied by the experimental data for semiconductors, a number of authors in this century, led by Born [9, 70], derived generalized Cauchy relations for noncentral forces in the diamond structure [10, 11].

Born's ingenious idea was to consider an *underdetermined* model (with fewer degrees of freedom than the number of independent elastic constants) and derive the implied elastic constant relations. If these relations are not satisfied, then the *functional form* cannot reproduce the data, no matter how it is fit. If they are satisfied, then we have compelling evidence that the functional form is correct. This kind of information is rare in the field of interatomic potentials; usually the validity of a functional form can only be assessed by fitting experience, which is time-consuming and inconclusive.

In this chapter we analyze the elastic properties of several general classes of many-body potentials in the diamond and graphitic crystal structures in order to gain insight into the mechanical behavior of sp^3 and sp^2 hybrid covalent bonds, respectively. These high symmetry atomic configurations must be accurately described by any realistic model of interatomic forces in a tetravalent solid. We only discuss results for three-body cluster potentials, ignoring bond order cluster functionals in the interest of simplicity. In this work the so-called Valence Force Field (VFF) models [50, 52], which can only describe small distortions of the diamond lattice, are also not considered. The goal in the VFF approach is to reproduce lattice dynamics as accurately as possible, paying little or no attention to broader transferability (with some exceptions [51, 52]). Over forty such potentials have been produced for Si alone [52], with the most recent displaying superb agreement with experiment for elastic constants and phonon frequencies [53]. However, as described earlier, unifying themes of this thesis are simplicity and transferability, and hence our motivation is quite different from VFF.

3.1 Taylor Expansion of the Cohesive Energy

The generic form of a three-body cluster potential is,

$$E = \sum_{i,j} \phi(R_{ij}) + \sum_{i,j} \sum_{k>j} \psi(R_{ij}, R_{ik}) h(l_{ijk}), \tag{3.1}$$

where we adopt the notation of Chapter 2. We make no assumptions about the functions ϕ, ψ and h (aside from differentiability, of course). Without loss of generality, we assume symmetry of the three-body radial function under exchange of atoms, $\psi(r_i, r_j) = \psi(r_j, r_i)$, which implies that $\psi_1 = \psi_2$ and $\psi_{11} = \psi_{22}$, where subscripts 1 and 2 on ψ indicate partial derivatives with respect to the first and second arguments. A natural class of symmetric radial functions is separable (like SW), $\psi(r_1, r_2) = g(r_1)g(r_2)$, but we do not require separability in this analysis. A trivial extension of the present model is to add more three-body terms of the same form, but with different angular and radial functions, as in the potential of Biswas and Haman [41]. This simply involves summation over all the three-body terms in all elastic constant formulae, so we shall not mention it again.

Now let us consider infinitesimal strains of a reference crystal structure. Assuming lattice symmetry and strain homogeneity, the energy per atom of the crystal is equal to the energy of a central atom, justifying the notation, $r_i = R_{0i}$ and $l_{ij} = l_{0ij}$. Using elementary calculus, the change in energy per atom for a three-body potential, expanded to second order in strain, is,

$$\begin{aligned}\Delta E &= \sum_i \left(\phi' \Delta r_i + \frac{1}{2}\phi'' \Delta r_i^2\right) \\ &+ \sum_i \sum_{j>i} \left[h \left(\psi_1(\Delta r_i + \Delta r_j) + \frac{1}{2}\psi_{11}(\Delta r_i^2 + \Delta r_j^2) + \psi_{12}\Delta r_i \Delta r_j\right)\right. \\ &\left. + h' \Delta l_{ij} \left(\psi + \psi_1(\Delta r_i + \Delta r_j)\right) + \frac{1}{2} h'' \psi \Delta l_{ij}^2 \right], \end{aligned} \tag{3.2}$$

where primes indicate derivatives, summation is over first neighbors, and all functions are evaluated in the unstrained, equilibrium state. The dependence of the quantities Δr_i and Δl_{ij} on strain must be computed separately for each crystal structure, which is tedious, but straight-forward. Therefore, we leave these unenlightening details to Appendix A, where the deformed bond lengths and angles are calculated for the independent strains for the diamond and graphitic lattices. Once these formulae are substituted into Eq. (3.2), the coefficients of linear terms must vanish, yielding equilibrium conditions, and those of the quadratic terms are the elastic constants.

The general form we are considering here has eight degrees of freedom for elastic properties: ϕ', ϕ'', $h\psi_1$, $h\psi_{11}$, $h\psi_{12}$, $h'\psi$, $h'\psi_1$ and $h''\psi$. In the cases of the SW and KP potentials, this number is reduced to two, ϕ'' and $h''\psi$, since $\phi' = h = h' = 0$. The Tersoff potentials, have many more degrees of freedom for elastic properties under the usual circumstances, and hence we will not be able to derive any implied dependencies. Elastic constant formulae for the related bond order potentials [21] and angularly-dependent embedded-atom potentials [72] have been calculated. These environment-dependent models have enough degrees of freedom to fit all the elastic constants (although none has managed to do so for Si, while preserving other important properties). Since our aim is to derive elastic constant relations, however, we will only consider simpler, underdetermined models.

3.2 Diamond sp^3 Hybrid Covalent Bonds

Due to the cubic symmetry of the diamond structure, there are only three independent elastic constants, C_{11}, C_{12} and C_{44}. The bond lengths and angles in Eq. (3.2) are related to the independent strains ε_1, ε_2 and γ_4 in Appendix A. After applying the equilibrium conditions, elastic constant formulae are derived by comparing with the definition,

$$V_d \Delta E = \frac{1}{2} C_{11}(\varepsilon_1^2 + \varepsilon_2^2) + C_{12}\varepsilon_1\varepsilon_2 + \frac{1}{2} C_{44}\gamma_4^2, \tag{3.3}$$

where $V_d = a^3/8$ is the volume per atom, which converts to the standard units of pressure. (a is the lattice constant.)

3.2.1 First Neighbor Interactions

With first neighbor interactions, the condition for equilibrium is

$$\phi' + 3\psi_1 h = 0, \tag{3.4}$$

which reduces the number of degrees of freedom to seven. If $h = 0$ (for the tetrahedral angle), then the pair potential must have a minimum at the first neighbor distance. At first we do not allow any internal relaxation. This has not effect on C_{11} and C_{12}, but C_{44} will be replaced by the unrelaxed value C_{44}^o. It turns out that the diamond elastic constants with a first-neighbor, three-body potential are:

$$V_d C_{11} = K + \frac{64}{27}\psi h'', \tag{3.5}$$

$$V_d C_{12} = K - \frac{32}{27}\psi h'', \tag{3.6}$$

$$V_d C_{44}^o = K + \frac{32}{81}\psi h'' - \frac{16}{9} r^2 \psi_{12} h - \frac{32}{27} r \psi_1 h + \frac{16}{27}\psi h', \tag{3.7}$$

where K is the bulk modulus,

$$V_d K = \frac{4}{9} r^2 [\phi'' + 3h(\psi_{11} + \psi_{12})], \tag{3.8}$$

and $r = \sqrt{3}a/4$ is the first neighbor distance. As a check, K can be derived from uniform dilation, and the relation $K = (C_{11} + 2C_{12})/3$ is satisfied. In the case of the

SW potential ($h = h' = 0$), we recover the formulae of Cowley, who also calculated phonon frequencies [71].

Requiring crystal stability places restrictions on the possible values of the degrees of freedom. Corresponding to the three independent modes of deformation [75], there are three inequalities,

$$\phi'' + 3h(\psi_{11} + \psi_{12}) > 0, \tag{3.9}$$

$$2\psi h'' - 9r^2\psi_{12}h - 6r\psi_1 h + 3\psi h' > 0, \tag{3.10}$$

$$\psi h'' > 0, \tag{3.11}$$

which stabilize the diamond lattice against uniform dilation ($K > 0$), simple shear of a cubic face ($C_{44}^o > 0$) and the second shear mode ($C_{11} - C_{12} > 0$), respectively. Internal relaxation can only lower the shear modulus ($C_{44} < C_{44}^o$), so the inequality of Eq. (3.10) can be strengthened using the formula for C_{44} derived below. In the important case, $h = 0$ and $\psi > 0$, the stability relations reduce to requirements of positive curvature for the pair potential and angular function, $\phi'' > 0$ and $h'' > 0$.

The only way to make our three-body cluster potential underdetermined for elastic properties is to assume $h = h' = 0$, like the SW and KP potentials. This general case is equivalent to a simple model of diamond elasticity proposed by Harrison in his Ph.D. thesis 30 years before SW [11, 12]. The Harrison model has two separate degrees of freedom, C_0 and C_1, for radial and angular forces [76], respectively, defined by the valence force field equation of Musgrave and Pope [77],

$$\Delta E = \frac{1}{2}\sum_i \frac{1}{2} C_0 \frac{\Delta r_i^2}{r^2} + \sum_i \sum_{j>i} \frac{1}{2} C_1 \Delta\theta_{ij}^2, \tag{3.12}$$

where the leading factor of 1/2 avoids double counting bonds and the sums are over first neighbors only. In terms of our cluster potential formalism, the Harrison force constants are,

$$C_0 \;=\; 2r^2\phi''(r), \tag{3.13}$$

$$C_1 \quad = \quad \frac{8}{9}\psi(r,r)h''(-1/3), \tag{3.14}$$

which follows by comparison of Eqs. (3.2) and (3.12), using $\Delta l^2 = (8/9)\Delta\theta^2$. One way to determine C_0 and C_1 is to reproduce the experimental values of C_{11} and C_{12}. In that case, the Harrison force constants for Si are $C_0 = 55.0$ eV and $C_1 = 3.2$ eV. The ratio C_0/C_1, 17.2 in the case of Si, is of the same order of magnitude in most tetrahedral semiconductors, indicating that radial forces are generally about ten times larger than angular forces [76].

In the early literature on elastic forces, unrelaxed elastic moduli were ignored, because they are not experimentally accessible. With the advent of *ab initio* calculations that predict elastic constants to within a few percent of experimental values, we can now analyze unrelaxed elastic properties as well. Since the Harrison model has two degrees of freedom for the three unrelaxed elastic constants, there is an implied relation,

$$4C_{11} + 5C_{12} = 9C_{44}^o, \tag{3.15}$$

which appears not to have been noted in previous studies (probably due to its experimental inaccessibility). As shown in Table 3.1, *the experimental and* ab initio *elastic constants for silicon satisfy this relation* within experimental and computational error. No other known elastic constant relation for covalent solids is satisfied with such precision, which is comparable to the nearly-perfect Cauchy relation $C_{12} = C_{44}$ in ionic solids [75]. This result unambiguously selects the Harrison model to describe diamond elasticity without internal relaxation. We also have an answer to one of our fundamental questions: it is indeed possible to perfectly reproduce a nontrivial manifold on the Born-Oppenheimer energy surface for covalent solids with a simple empirical potential.

On the other hand, more general cluster potentials and functionals, including the Tersoff, BH and PTHT formats, do not require our relation, and appear to be unable to satisfy it under the usual circumstances. This is demonstrated in Table 3.1 and explains why it has proven difficult to obtain good elastic properties with the Tersoff

	EXPT	LDA	SW	BH	T2	T3	DOD	PTHT	TB
C_{11}	1.67		1.617	2.042	1.217	1.425	1.206	2.969	1.45
C_{12}	0.65		0.816	1.517	0.858	0.754	0.722	2.697	0.845
C_{44}	0.81		0.603	0.451	0.103	0.690	0.659	0.446	0.534
C^o_{44}		1.11	1.172	1.049	0.923	1.188	3.475	2.190	1.35
α_B	1.07		1.11	1.03	0.33	0.28	0.71	0.93	0.11
α_H	1.16		1.00	0.98	2.99	2.31	1.69	1.71	2.80
α_{new}	0.99		1.00	1.67	1.10	0.89	0.27	1.29	0.82

Table 3.1: Comparison of elastic constants (in Mbar) for diamond cubic silicon computed with empirical models and the experimental (EXPT) or *ab initio* (LDA) values. The values for EXPT are from Simmons and Wang [78], for LDA from Nielsen and Martin [79] for tight-binding (TB) from Bernstein and Kaxiras [80] and for the empirical potentials Biswas-Haman (BH), Tersoff (T2, T3), Dodson (DOD) and Pearson-Takai-Halicioglu-Tiller (PTHT) from Balamane *et al* [19]. The Stillinger-Weber (SW) values are calculated with the analytic formulae of Cowley [71] and scaled to set the binding energy to 4.63 eV [19]. In the lower half of the table, the Born [9], Harrison [12] and new elastic constant relations are tested by calculating the ratios $\alpha_B \equiv 4C_{11}(C_{11}-C_{44})/(C_{11}+C_{12})^2$, $\alpha_H \equiv (7C_{11}+2C_{12})C_{44}/3(C_{11}+2C_{12})(C_{11}-C_{12})$ and $\alpha_{new} \equiv (4C_{11}+5C_{12})/9C^o_{44}$.

potential. Note that the T3 angular function[38], which was specifically optimized for elastic properties, resembles the SW angular function, while the other versions do not. Moreover, only the T3 angular function agrees with the theoretical predictions of the quantum-mechanical bond order expansion [21, 67]. These results suggest that it may be important for the angular function to at least approximately have a minimum of zero at the tetrahedral angle within the Tersoff format too. We shall return to this issue in the next section, when we consider a quantum mechanical approximation related to the Tersoff potential.

Let us now turn to the third experimental elastic constant, C_{44} with internal relaxation. Since the Harrison model has only two degrees of freedom for this case too, it is interesting to see if it can reproduce more elastic properties. By lattice symmetry, the only possible relaxation of the two interpenetrating FCC lattices for a yz (γ_4) shear is to squeeze them together in the x direction. The driving force for internal relaxation is the resistance to stretching of sp^3 bonds, so following Kleinman we parameterize the relaxation by moving one of the two basis atoms by $a\zeta\gamma_4/4$ in the positive x direction. If $\zeta = 1$, then all bond lengths are unchanged at first order in the strain, and if $\zeta = -1/2$ the angles are unchanged, as shown in the Appendix A [81, 76]. The shear constant of the Harrison model is

$$V_d C_{44}(\zeta) = \frac{4}{9}(1-\zeta)^2 r^2 \phi'' + \frac{32}{81}(1+2\zeta)^2 \psi h'', \tag{3.16}$$

where the value of ζ is determined by minimization ($dC_{44}/d\zeta = 0$),

$$\zeta = \frac{9r^2\phi'' - 16\psi h''}{9r^2\phi'' + 32\psi h''} = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}, \tag{3.17}$$

which can be viewed as another elastic constant relation implied by the Harrison model. This one, however, is not satisfied quite so well. Using the most recent experimental value $\zeta = 0.72 \pm 0.04$ [82], the ratio of the left to the right hand side of Eq. (3.17) is 0.74, indicating that the predicted ζ is about 25% too small with the Harrison model. Earlier studies report values of ζ between 0.62 and 0.75 (which are all consistent in light of the error bounds) [83, 84, 82]. With these values, the discrepancy with the Harrison model may be as small as 14%, but in any case the model clearly somewhat underpredicts ζ.

Substituting Eq. (3.17) into Eq. (3.16), we obtain a formula for C_{44} with the Harrison model. Since there are still only two degrees of freedom for the three experimental elastic constants, there is another implied relation, originally derived by Harrison [12],

$$(7C_{11} + 2C_{12})C_{44} = 3(C_{11} + 2C_{12})(C_{11} - C_{12}). \tag{3.18}$$

The experimental elastic constants satisfy the Harrison relation to within 16% (not quite as well as the Born relation). In contrast, notice once again that the Tersoff format potentials, T2, T3 and Dodson (DOD) [44], are far from satisfying this relation, as shown in Table 3.

The performance of the Harrison model is impressive, since it is quite underdetermined for elastic properties. It provides a reasonable description of five elastic properties (C_{11}, C_{12}, C_{44}, C_{44}^o and ζ) with only two degrees of freedom. Let us now see how far the functional form can be pushed. Combining Eqs. (3.18) and (3.15), we arrive at a relation involving all four elastic constants,

$$C_{44}^o - C_{44} = \frac{(C_{11} + 8C_{12})^2}{9(7C_{11} + 2C_{12})}, \tag{3.19}$$

that expresses the effect of internal relaxation. In the case of Si, if the two degrees of freedom in the Harrison model are used to reproduce the experimental values of C_{11} and C_{12}, and thus also C_{44}^o by Eq. (3.15), then the predicted value of C_{44} from Eq. (3.19) is 0.71 Mbar, which is only 12% smaller than the experimental value of 0.81 Mbar. This explains the surprising fact [19] that the SW potential gives one of the best descriptions of elastic properties in spite of not having been fit to any elastic constants. We conclude that it is the superiority of the simple SW functional form that gives the desirable properties, not a complex fitting procedure.

Using analytic expressions for the elastic constants it is possible to devise a simple prescription to achieve good elastic properties with the Harrison model [76]. As a simple consequence of $h = 0$, the curvature of the pair potential is given by,

$$\phi''(r_d) = \frac{3V_d}{4r_d^2}(C_{11} + 2C_{12}). \tag{3.20}$$

The curvature of the angular function can be related to the second shear modulus,

$$g(r_d)^2 h''(-1/3) = \frac{9V_d}{32}(C_{11} - C_{12}). \tag{3.21}$$

Using the *ab initio* data for Si in Table 3.1, the right hand sides of Eqs. (3.20) and (3.21) evaluate to 8.1 eV/Å^2 and 5.7 eV, respectively. This provides a simple two-step procedure to maintain good elastic behavior while fitting any potential reducing to the Harrison model near the diamond lattice: (i) scale the pair interaction $V_2(r)$ to obtain the correct bulk modulus $K = (C_{11} + 2C_{12})/3$, and (ii) scale the three-body energy to set the second shear modulus. As shown above, this will lead to perfect unrelaxed elastic constants and only a 12% error in C_{44} for Si. The structural relaxation will not be as accurate, with $\zeta = 0.529$, smaller than the experimental values by 15–30%, but the overall elastic properties are still excellent, much better than might be expected *a priori* from such a simple functional form.

3.2.2 Quantum-Mechanical Interpretation

With our new results, we can better understand the successes and failures of the Harrison model, at least in the case of Si. The most important result is that the Harrison model reproduces all the unrelaxed elastic constants, not just C_{11} and C_{12} as is generally believed based on its two degrees of freedom. Therefore, the discrepancy in satisfying the Harrison relation with the experimental elastic constants is due to an inadequate description of C_{44} with internal relaxation. We may conclude that the model does not respond correctly to changes in the atomic environment that occur during relaxation. Chelikowsky's dangling bond vector, defined in Eq. (2.5), is a convenient variable to control such environment dependence because it vanishes (for any strain) in the absence of internal relaxation.

These findings have important implications for the theory of covalent bonding in solids. A natural connection between our empirical models and a quantum mechanical treatment of the electrons is supplied by the Bond Order Potential (BOP) expansion of the total energy within the Tight Binding (TB) model [67, 20, 62, 63], through the elasticity analysis of Alinaghian, Nishitani and Pettifor [21]. The BOP angular dependence for σ-bonding,

$$\begin{aligned} h_\sigma(\theta) &= a + b\cos(\theta) + c\cos(2\theta), && (3.22)\\ a &= 1 - b - c, && (3.23)\\ b &= \frac{2p_\sigma}{(1+p_\sigma)^2}, && (3.24)\\ c &= \frac{p_\sigma^2}{(1+p_\sigma)^2}, && (3.25) \end{aligned}$$

is controlled by a single quantum mechanical quantity, $p_\sigma = pp\sigma/|ss\sigma|$, which is the ratio of TB hopping matrix elements between p orbitals pointing toward each other ($pp\sigma$) and between spherically-symmetric s orbitals ($ss\sigma$) centered on neighboring atoms [21]. If $p_\sigma = 0$, the angular function is completely flat, $h_\sigma(\theta) = 1$, consistent with the nondirectionality of a pure s bond. In order to better understand the BOP angular function for $p_\sigma > 0$, let us cast it in a more transparent form,

$$h_\sigma(\theta) = \left(\frac{p_\sigma}{1+p_\sigma}\right)^2 \left(\cos(\theta) + \frac{1}{p_\sigma}\right)^2. \qquad (3.26)$$

At the other extreme, the angular function for $p_\sigma = \infty$, $h_\sigma(\theta) = \cos^2(\theta)$, has a narrow, symmetric minimum at 90°, indicating that an orbital on a neighboring atom interferes (overlaps) least with a pure p bond when it is perpendicular to the bond axis. The intermediate case, $p_\sigma = 3$, corresponds to an ideal sp^3 hybrid bond, and naturally the angular function has a minimum of zero at the tetrahedral angle[1]. Therefore, when $p_\sigma = 3$, BOP reduces to the Harrison model, as far as elasticity is concerned.

[1]The $p_\sigma = 3$ angular function, $h_\sigma(\theta) \propto (\cos(\theta) + 1/3)^2$, is actually identical to the SW angular function, but angular dependence enters the functional form differently in BOP and SW, so there is little similarity away from the diamond lattice.

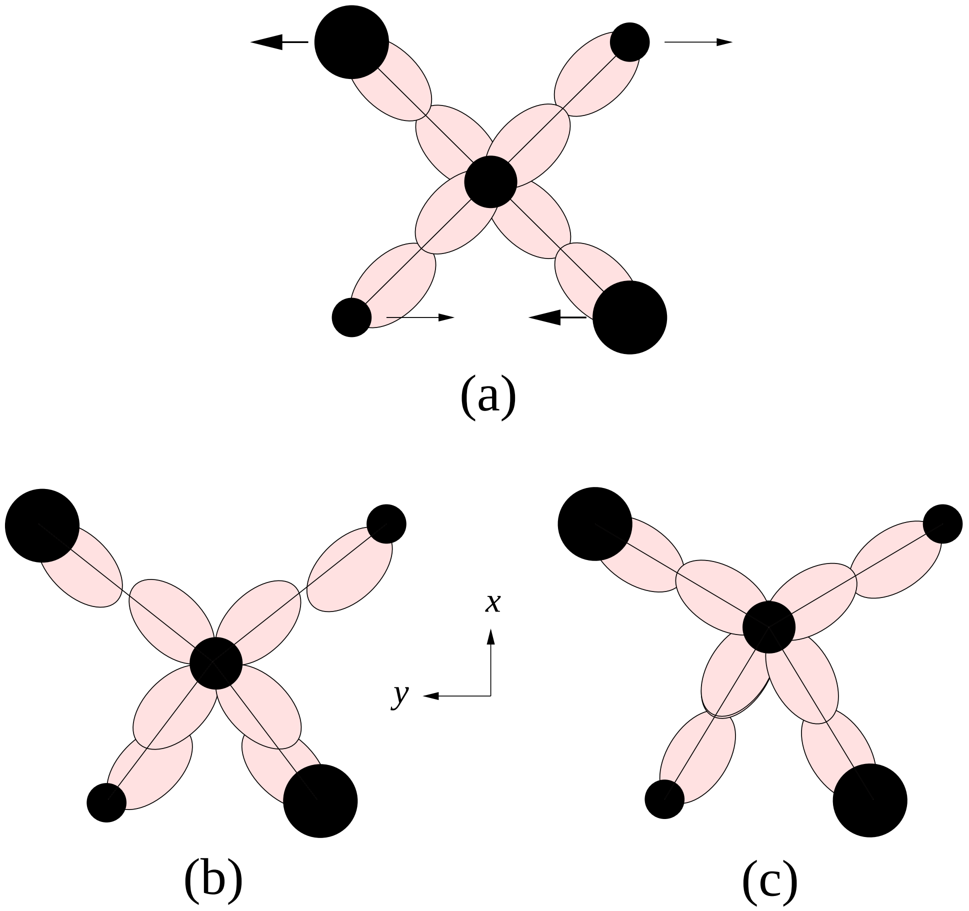

Figure 3.1: Quantum-mechanical effects during tetragonal yz (C_{44}) shear of the diamond lattice. The size of an atom (solid circle) suggests its position in the z direction out of the page. The equilibrium tetrahedron is shown in (a) with filled ellipses representing sp^3 hybrid orbitals. The strained state without relaxation is shown in (b) with rigid sp^3 hybrids, which we prove to be an accurate picture, at least for Si. The effects of internal relaxation in the x direction and rehybridization are shown in (c).

This gives us a connection with quantum mechanics: The success of the Harrison model for unrelaxed elasticity validates the Rigid Hybrid Approximation, in which electrons stay frozen in the ideal sp^3 orbitals as the lattice is deformed [76]. Harrison and Phillips showed that this approximation works well for the second shear constant $C_{11} - C_{12}$ in C, Si and Ge [86], but the implication here is that *the Rigid Hybrid Approximation accurately describes all elastic deformations without internal relaxation in Si.*

This result is somewhat surprising since rehybridization is possible even without internal relaxation [76]. For example, in the case of the C_{44} shear shown in Fig. 3.1, the content of the $|p_x>$ orbital at each atom may be reduced in two hybrids, whose mutual angle is opening, and increased in the other two, whose mutual angle is closing, with compensating changes in the $|s>$ content of each hybrid to maintain orthogonality. (The $|p_y>$ and $|p_z>$ contents will not change due to lattice symmetry.) These shifts tend to align the hybrid orbitals better with the bond axis, presumably lowering the energy of the bonding state due to the greater wavefunction overlap. At least in the case of Si, however, our results suggest that such rehybridization is minimal if relaxation of the atomic positions is suppressed.

Internal relaxation is driven by the aversion to bond stretching, which is much greater than bond bending resistance (because $C_0/C_1 \gg 1$). As shown in the figure, atomic displacements in the x direction keep bond lengths close to the equilibrium value. In the Harrison model, the relaxation distance is reached when these radial forces are balanced by angular forces that increase with the displacement. The likelihood of rehybridization is increased by relaxation, since the misalignment of the ideal hybrids is exaggerated. With the rigid hybrid interpretation given above, the inadequacy of Harrison model describing C_{44} and ζ may be seen as evidence of rehybridization during internal relaxation.

The BOP expansion may provide a convenient framework to understand this phenomenon. The transfer of probability density from $|p_x>$ to $|s>$ described above correlates with a change in p_σ. An increase in p_σ reduces the minimum of the angular function for the two bonds subtending the closing angle, and similarly, a decrease in p_σ increases the favored angle for the other two opening bonds[2]. Therefore, each bond may change its preferred angle to adapt to its environment, suggesting an *angular* driving force for relaxation that might explain why the Harrison model underestimates ζ. The angular force constant in the BOP expansion is proportional to $h''_\sigma = 2[p_\sigma/(1+p_\sigma)]^2$, so if rehybridization occurs as discussed above, the angular force constant is increased for half of the angles and decreased for the other half. The net effect of rehybridization on C_{44} is then unclear because we do not know the precise values in p_σ during relaxation, but it is certain that the rigid hybrid approximation fails.

In the elasticity analysis of Alinaghian *et. al.* a single value of p_σ without environment-dependence is used [21]. It turns out that the choice $p_\sigma = 2$ improves the prediction of C_{44} for a wide range of covalent solids compared with $p_\sigma = 3$ (see Fig. 3 of Ref. [21]). This choice lies in between the theoretically determined p_σ values of 1.57 [87] and 2.31 [76] for Si. Our results, however, imply that a BOP with $p_\sigma = 3$ should be able to fit C_{11}, C_{12} and C^o_{44} for Si. We may conclude that the quantum-mechanical parameter p_σ, and hence the angular function, should depend on the bonding environment, perhaps measured by the Chelikowsky vector, to mimic the effect of rehybridization by varying the angular force constant and the preferred angle for each bond during internal relaxation.

3.2.3 Second Neighbor Interactions

In the spirit of simplicity, let us consider extending the pair potential, but the not the three-body interaction, to include second neighbors. This already introduces two more

[2]Note that shifting the minimum of the angular function also incurs a competing penalty for the four angles per atom that do not change at leading order.

degrees of freedom, $R\phi'(R)$ and $R^2\phi''(R)$, where R is the second neighbor distance. With second neighbor forces, the pair potential does not generally have a minimum at the first neighbor distance. The new equilibrium condition is,

$$r\phi'(r) + 3R\phi'(R) + 3r\psi_1(r,r)h(-1/3) = 0. \tag{3.27}$$

Using the geometrical strain information from Appendix A, the contributions to the (unrelaxed) elastic constants from second neighbor pair interactions are ($\Delta C = C - C_{first}$):

$$\begin{aligned} V_d \Delta C_{11} &= \frac{8}{9} r\phi'(r) + 2R\phi'(R) + 2R^2\phi''(R), & (3.28)\\ V_d \Delta C_{12} &= -\frac{4}{9} r\phi'(r) - R\phi'(R) + R^2\phi''(R), & (3.29)\\ V_d \Delta C_{44}^o &= \frac{2}{9} r\phi'(r) + R\phi'(R) + R^2\phi''(R), & (3.30)\\ V_d \Delta K &= \frac{4}{3} R^2\phi''(R). & (3.31) \end{aligned}$$

It might seem that by symmetry we do not need to consider internal relaxation because the second neighbors are part of the same Bravais lattice (FCC) as the central atom and first neighbor relaxation has already been computed. However, this is not so for a subtle reason: due to the equilibrium condition, $\phi'(r) \neq 0$, and thus our old formulae for ζ and C_{44} are incorrect in this case.

To proceed with internal relaxation, we assume the Harrison format for first neighbor interactions with the additional radial second neighbor forces, which we shall call the H2 model. The change in shear constant of the H2 model (compared to the first neighbor Harrison model) is,

$$V_d \Delta C_{44} = \frac{2}{9} r\phi'(r)[3 + 6\zeta^2 - 2(1-\zeta)^2], \tag{3.32}$$

where the Kleinman internal strain parameter changes nonlinearly,

$$\zeta = \frac{9r^2\phi''(r) - 16\psi(r,r)h'' - 9r\phi'(r)}{9r^2\phi''(r) + 32\psi(r,r)h'' + 18r\phi'(r)}. \tag{3.33}$$

Since the H2 format has four degrees of freedom, it may be able to reproduce the four elastic constants, and the Kleinman parameter could then provide a fair test of the functional form. Since the relation of Eq. (3.15) already agrees with experiment, the deviations introduced by second neighbor forces must also satisfy it, $4\Delta C_{11} + 5\Delta C_{12} = 9\Delta C_{44}^o$. Solving for the values of the four parameters that exactly reproduce the four elastic constants is a nonlinear inverse problem (due to C_{44}). Harrison has apparently found the solution numerically [12], which would prove that with second neighbor radial forces the Harrison format can be extended to fit all the elastic constants.

Let us check if a simpler model with fewer parameters can still fit the data. The simplest second neighbor model we can make assumes $\phi'(R) = 0$, which we shall call the H2' model. Since we still assume $h = 0$ from the Harrison model, the equilibrium condition implies $\phi'(r) = 0$ as well. Thus, in the H2' model the pair potential is flat at both the first and second neighbor distances. The H2' model has three degrees of freedom, C_0 and C_1 from the Harrison model and a new parameter defined by,

$$V_d C_2 = R^2 \phi''(R). \tag{3.34}$$

Therefore, there is one implied elastic constant relation (which generalizes the Harrison relation), namely

$$(7C_{11} + 2C_{12} - 16C_2)(C_{44} - C_2) = 3(C_{11} + 2C_{12} - 4C_2)(C_{11} - C_{12} - C_2). \tag{3.35}$$

The third degree of freedom can be expressed in terms of the discrepancy in satisfying Eq. (3.15),

$$C_2 = \frac{1}{4}(9C_{44}^o - 4C_{11} - 5C_{12}), \tag{3.36}$$

which vanishes for the (first neighbor) Harrison model. Using the experimental and *ab initio* data for Si from Table 3.1, $C_2 = -0.015$, which is very small due to the nearly perfect unrelaxed elastic constants of the Harrison model. The implication is that *second neighbor forces are very weak in the diamond structure for Si.* In the particular case of the H2' model, second neighbor radial forces are 100 times weaker than angular forces, $C_2/C_1 = 0.014$, and over 1000 times weaker than first neighbor radial forces, $C_2/C_0 = 0.00031$. It is likely that other models would also predict weak second neighbor forces. This is consistent with the fact that the *ab initio* (111) stable stacking fault energy in Si, 0.005 eV/Å^2 = 0.036 eV/atom, is over 100 times smaller than the binding energy, $E_{ssf}/E_b = 0.0078$. (The atomic arrangement of first neighbors in the (111) stable stacking fault is identical to the perfect crystal).

Although second neighbor forces are small in the diamond structure, they are nevertheless important for certain materials processes. For example, the equilibrium separation of partial dislocations is determined by a balance between long-range elastic repulsion and stable stacking fault energy. So, let us continue to investigate relevance of the three constant H2' model. In addition to the elastic constant relation above, there is also a relation involving the Kleinman parameter,

$$\zeta = \frac{C_{11} + 8C_{12} - 10C_2}{7C_{11} + 2C_{12} - 16C_2}. \tag{3.37}$$

With the *ab initio* and experimental data for Si, the ratios of the left to the right hand sides of Eq. (3.35) and Eq. (3.37) are 1.16 and 0.74, respectively. In a fair test, the H2' model does not perform any better than the simpler Harrison model, thus invalidating its assumptions.

This leads us to an interesting general conclusion: adding degrees of freedom does not necessarily help fit *ab initio* data if the *functional form* is inappropriate, which is consistent with our observations about the Tersoff potentials. This also supports our suggestion in Chapter 2 that simple, theoretically motivated functional forms are superior to flexible fitting strategies. We also see the power of elastic constant relations: we are able to discard a functional form without ever having to do any fitting. Of course, this form may still be fortuitously successful for other properties, so fitting is still needed to check overall transferability. The primary value of theoretical results like elastic constant relations is in providing much needed guidance for fitting.

3.3 Graphitic sp^2 Hybrid Covalent Bonds

We can also obtain useful information about interatomic forces due to sp^2 hybrid bonds from the elastic moduli of the graphitic structure. In the following analysis, we neglect interplanar interactions, which are insignificant compared to the covalent bonds within a single, hexagonal plane. For example, the out-of-plane elastic constants C_{13} and C_{33} in graphite (carbon) are two orders of magnitude smaller than the in-plane constant C_{11} [88]. An isolated, hexagonal plane has two independent elastic constants, C_{11} and C_{12} with units of energy per unit area (and $C_{66} = (C_{11} - C_{12})/2$) [85]. Since a hexagonal plane is only a hypothetical bonding state for Si, too large in energy to be observed experimentally, we must perform *ab initio* calculations to obtain the elastic constants.

3.3.1 *Ab Initio* Elastic Constants for Graphitic Silicon

For reasons given above, it is sufficient for our purposes to consider an isolated hexagonal plane. Our *ab initio* calculations involve density functional theory in the local density approximation (LDA) using a plane wave basis with a 12 Ry cutoff and 1296 points in the full Brillouin zone for reciprocal space integrations. (These choices guarantee sufficient accuracy.) In order to preserve periodic boundary conditions, the out-of-plane lattice parameter is fixed at $c = 5.5$ Å, which is large enough to ensure neglible interplanar forces. As shown in Fig. 3.2, great care must be exercised in locating the parabolic regime of energy versus strain, to which the elastic constants (curvatures) are very sensitive. In each case, the region of linear elasticity is identified (typically strains less than 3%) using the χ^2 statistic, to measure goodness of parabolic fit. The best fit parabola is then used to approximate the elastic constant. Our results are $C_{11} = 1.79$ Mbar and $C_{12} = 0.51$ Mbar.

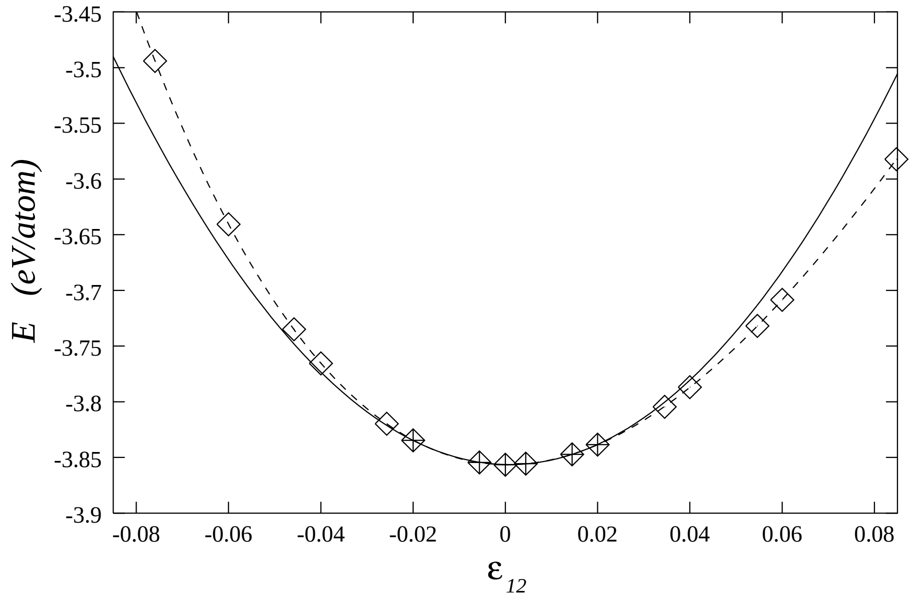

Figure 3.2: *Ab initio* (LDA) data points (diamonds) for energy versus strain of stacked hexagonal planes with $c = 5.5$ Å. The dashed line is a fit of all the data with a sixth order polynomial. The solid line is a parabola fit to the linear elastic points (+).

3.3.2 First Neighbor Interactions

Using the geometric formulae from Appendix A, we can compute the elastic constants of three-body potentials as we did for the diamond case. Since there are only two nonzero elastic constants, we should keep the functional form as simple as possible, and thus we restrict ourselves to only first neighbor interactions. The equilibrium condition for the hexagonal plane is,

$$\phi' + 2h\psi_1 = 0, \tag{3.38}$$

and using it to cancel terms, the elastic constants are:

$$A_h C_{11} = \frac{9}{8}(r^2\phi'' + 2r^2\psi_{11}h + r^2\psi_{12}h - r\psi_1 h') + \frac{9}{16}\psi h' + \frac{27}{32}\psi h'', \tag{3.39}$$

$$A_h C_{12} = \frac{3}{8}r^2\phi'' + \frac{3}{4}r^2\psi_{11}h + \frac{15}{8}r^2\psi_{12}h + \frac{9}{8}r\psi_1 h' - \frac{15}{16}\psi h' - \frac{27}{32}\psi h'', \tag{3.40}$$

where $A_h = a_h^2\sqrt{3}/4$, a_h is the in-plane lattice constant and all quantities are evaluated at the equilibrium bond length $r_h = a_h/\sqrt{3}$ and angle $l = -1/2$. Consistent with symmetry requirements, $C_{44} = \frac{3}{2}r\phi' + 3r\psi_1 h = 0$, for any fist neighbor, three-body potential. However, the vanishing value of C_{44} only occurs at equilibrium, and there are still nonzero radial and angular distortions for the γ_4 shear (all at second order).

As in the diamond case, let us consider the additional simplification, $h = h' = 0$, only now these conditions apply to the *hexagonal angle* 120°. We are effectively applying the Harrison model to three-fold coordinated sp^2 bonds. This idea, proposed by Kaxiras and also suggested by Khor and Das Sarma [45], is discussed in greater detail in Chapter 5, and for graphitic elasticity we call it the K model. The K model is justified by the BOP expansion in the Rigid Hybrid Approximation, since sp^2 hybrids have $p_\sigma = 2$ and the BOP angular function, $h_\sigma(\theta) = (4/9)(\cos(\theta) + 1/2)^2$, has a minimum of zero at the hexagonal angle in that case.

Like the Harrison model for diamond, the K model has two degrees of freedom, $r^2\phi''$ and $\psi h''$. Since there are only two elastic constants, we do not get a dependency relation, but by requiring crystal stability (equivalently, $h'' > 0$), we obtain the inequality, $C_{11} > 3C_{12}$. Using our *ab initio* data for Si, $C_{11} - 3C_{12} = 0.26$ Mbar > 0. Thus, the K model survives a test of its validity. Consistent with this result, the success of the Harrison format for sp^3 bonds makes it seem reasonable to use the same approach of the K model for sp^2 bonds, providing a unified view of covalent bond bending and stretching in the most common hybridizations.

A much more stringent test of the K hypothesis would involve calculating the elastic constant for another physically important deformation to provide a third piece of data, thus making the model underdetermined and implying a relation. For example, the hexagonal plane could be distorted out of the plane inhomogeneously, by moving one basis atom in the z direction while keeping the other fixed, which would introduce ripples into the plane resembling the ideal (111) surface. This could also be done with relaxation of the area of the plane, thus defining a generalization of the Kleinman parameter that would quantify the balance between bond-bending and bond-stretching forces in a graphitic plane. Such calculations would test the ability of the K model to describe out-of-plane bending of sp^2 bonds (to complement C_{11} and C_{12} which test in-plane bending), and would provide a means to unambiguously confirm or reject the K hypothesis for a given material. From our experience with the diamond lattice, it is likely that environment-dependence will be needed.

3.4 Comparison of sp^2 and sp^3 Bonds

The unified treatment of sp^2 and sp^3 hybrid covalent bonds with the Harrison and K models invites us to make comparisons of radial and angular stiffnesses. The relative radial stiffness is given by a simple ratio of elastic constants,

$$\frac{\phi_h''(r_h)}{\phi_d''(r_d)} = \frac{8r_d^2}{9r_h^2}\frac{A_h(C_{11}+C_{12})_h}{V_d(C_{11}+2C_{12})_d}, \tag{3.41}$$

where the subscript h refers to the equilibrium hexagonal plane with area per atom $A_h = a_h^2\sqrt{3}/4$, and d refers to the diamond lattice. For most covalent solids, the prefactor, $8r_d^2/9r_h^2$, is close to 1.0 (using the *ab initio* result for Si, $r_h = 2.23$Å, it is 0.99), so the elastic constant ratio on the right hand side of Eq. (3.41) provides a direct comparison of sp^2 and sp^3 radial forces. Our *ab initio* value of that ratio is 1.4 ± 0.1, implying that sp^2 bonds have 40% greater radial stiffness than sp^3 bonds in Si. The same result also follows directly from inverted pair potentials for the graphitic and diamond structures as described in Chapter 4.

A similar elastic analysis yields an expression for the relative angular stiffness of sp^2 and sp^3 hybrid bonds,

$$\frac{h_h''(-1/2)}{h_d''(-1/3)} = \frac{256 g_d(r_d)^2}{243 g_h(r_h)^2}\frac{A_h(C_{11}-3C_{12})_h}{V_d(C_{11}-C_{12})_d}, \tag{3.42}$$

Using our *ab initio* data for Si, we have, $g_h(r_h)^2 h_h''(-1/2)/g_d(r_d)^2 h_d''(-1/3) = 0.46 \pm 0.15$. Assuming $g_d(r) \approx g_h(r)$ with each function decreasing in accordance with inversion results (Chapter 4), then the prefactor, $256g_d(r_d)^2/243g_h(r_h)^2$, is nearly unity. In that case the ratio of elastic constants on the right hand side of Eq. (3.42) allows us to quantify the relative bending strength of the hybrid bonds. The *ab initio* value for the ratio of 0.44 ± 0.15 indicates that the angular stiffness of sp^2 bonds is smaller than that of sp^3 bonds in Si by about a factor of two, in spite of the greater radial stiffness of sp^2 bonds. This is consistent with the flatter angular function for $p_\sigma = 2$ than $p_\sigma = 3$ in the BOP expansion discussed above [21]. Our conclusion for the relative bending strength of sp^2 and sp^3 hybrids would be reversed only if $g_g(r_g)$ were smaller than $g_d(r_d)$ by at least a factor of two, which seems unlikely in light of the bond orders. No author has proposed this theoretical idea, so elastic constant analysis is leading us in a nonintuitive direction.

3.5 Conclusion

In summary, we have followed in the footsteps of Born in deriving elastic relations implied by simple functional forms of interatomic forces in covalent solids and have applied them to the case of silicon. Using *ab initio* calculations, the set of elastic constant data has been extended to include C_{44}^o for diamond and C_{11}, C_{12} and C_{44} for graphitic, which allows us to go beyond early studies restricted to experimental data (only C_{11}, C_{12} and C_{44} for diamond). The enlarged data set leads to new elastic constant relations. A surprising and important result is that the relation, $4C_{11} + 5C_{12} = 9C_{44}^o$, implied by the Harrison model is almost perfectly satisfied by the data for silicon, which is the first time such agreement has been discovered for a covalent material. We have interpreted the success of the Harrison model in terms of the Rigid Hybrid Approximation, which is apparently valid in Si for *any* elastic deformation without internal relaxation. We have also argued that weak environment-dependence, perhaps controlled by the Chelikowsky vector, is needed in the angular function to describe rehybridization. We have also suggested that second neighbor radial forces (the H2 model) can improve the Harrison model for the diamond structure, but a special case (the H2' model) having only one additional degree of freedom does not help at all.

In the case of the graphitic structure, we have found that a modified Harrison model (the K model) is consistent with the *ab initio* data for silicon, suggesting that a hybrid covalent bond (sp^3 or sp^2) is well represented by a separable, first-neighbor, three-body cluster potential whose angular function has a minimum of zero at the appropriate angle (109.47° or 120°, respectively). The strength of the angular forces is also different for the two hybrids. These results once again suggest the importance of environment-dependence in the angular function, this time depending strongly upon the *coordination*, a novel feature we shall incorporate into a model for silicon in Chapter 5. An environment-dependent angular function implies at least four-body interactions, which is consistent with quantum-mechanical predictions discussed in the previous chapter.

In addition to testing functional forms of interatomic potentials, elastic constant formulae provide quantitative guidance for fitting. Elastic constants for the diamond structure determine parameters in the potential, like the curvatures of the pair and angular functions in the Harrison model. The graphitic results allow direct comparison of sp^2 and sp^3 hybrids, which is useful in designing the environment dependence of the angular function.

Using analytic techniques and *ab initio* calculations, we have explored interatomic forces mediated by sp^2 and sp^3 covalent bonds. These results, however, say nothing of environment dependence and angular forces for more complicated structures involving overcoordination and metallic bonding (which are important for high-pressure crystal phases and the liquid). One wonders if such information could somehow be extracted directly from first principles data.