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A valence force field for diamond from *ab initio* molecular orbital cluster calculations

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Abstract. The lattice dynamics and elastic moduli of diamond are reinvestigated using a method based upon an *ab initio* valence force field obtained for the neopentane molecule. The calculated phonon dispersion relations are in very good agreement with experiment particularly with respect to the LA, LO, TO vibrational modes. The results demonstrate the transferability of force fields from *ab initio* calculations on suitably chosen molecular clusters to condensed phases, and also show that a five-parameter valence force field model is sufficient to reproduce most of the features of the lattice dynamics of diamond. Excellent agreement was found between calculated and experimental bulk moduli indicating adequate modelling of the bond stretching interactions. Deviations of the transverse acoustical vibration modes at low frequencies and the remaining elastic moduli are associated with bond angle interaction terms, which may be due to the omission of a longer range interaction force constant.

1. Introduction

There have been many theoretical studies of the elastic and vibrational properties of diamond [1–13] and materials with the diamond structure [6–16]. In many, an empirical force field has been fit to experimental elastic moduli and vibrational spectra and then used to calculate other properties of the material. However, it is desirable to develop methods to directly predict significant features of vibrational and elastic behaviour with minimal experimental input and based simply on structure-bonding concepts. Among others, Louie [11] conducted a non-empirical study of the vibrational and elastic properties of diamond using an *ab initio* pseudopotential and frozen phonon method. The results were very good although the calculation was quite involved. We were interested in exploring the usefulness of a somewhat simpler approach. This involved a very local force field model of diamond without involving explicit definitions of long range interactions. Our objective was to determine how well this could describe the vibrational and elastic properties of diamond.

Our method was based upon a model proposed by Musgrave and Pople [2]. These authors attempted to model the lattice dynamics of diamond using a valence force field derived from experimental data for the molecule neopentane, $C(CH_3)_4$. Their calculation was not successful at that time due to the incomplete nature of the experimentally derived molecular force field and inconsistencies in experimental values for

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Table 1. Calculated [17] and scaled neopentane internal and valence force constants used.

		Calculated (N m^{-1})	Scaled (N m^{-1})
$A_1(r)$	$F_{1,1}$	532.87	436.4
$E(\alpha)$	$F_{5,5}$	50.05	42.2
$T_2(r)$	$F_{13,13}$	462.24	387.4
T_2	$F_{13,14}$	35.26	36.6
$T_2(\alpha)$	$F_{14,14}$	57.84	47.5
	k_r	479.90	399.7
	k_{rr}	17.66	12.2
	$k_{r\theta}$	35.26	36.6
	k'_θ	53.95	44.8
	k''_θ	57.84	47.5

the elastic moduli of diamond. More recently, however, two of us, Guth and Hess [17], carried out an *ab initio* molecular orbital calculation for neopentane and obtained a full harmonic force field for this molecule using a polarised, split-valence (6-31G*) basis set. These non-empirical force constants gave frequencies in good agreement with experiment.

In the present study, we have taken the force constants for the tetrahedral (C_5) portion of neopentane from the *ab initio* study to obtain a non-empirical, five-parameter valence force field for diamond. Our objective was to test the hypothesis of Musgrave and Pople and, thereby demonstrate the value of modelling the vibrational and elastic properties of diamond using calculations on molecular fragments which possess similar symmetry. We have calculated dispersion curves based upon this model but independent of experimental data on diamond itself. However, since there are always some systematic errors in the type of calculations conducted, we also explored the value of scaling our results to parallel calculations on CF_4 which is isoelectronic with neopentane. Very reliable experimental force constants are available for CF_4 which, when compared to our calculated values, allow us to reasonably estimate the calculational errors.

We do not attempt in this study to make direct comparisons to force constants derived from other studies. The reason is that other models involved different definitions of the force constants. Our calculations do not omit certain symmetry constraints on the force constants as had been in some other investigations. In addition, force constants reported from many investigations typically were derived through analytical regression of experimental data. Due to the nature of the experimental data, determinations of unique sets of parameters are often not possible. On the other hand, *ab initio* treatments such as we use here allows for the determination of parameters which are unique as far as the specific model is concerned.

2. Procedure

The valence force field is defined as follows. For a tetrahedral arrangement of atoms there are five independent valence force constants which are related to the seven force constants below through redundancy conditions:

k_r is a bond stretching constant for nearest neighbours;

f_θ is an angle bending constant;

Table 2. Calculated (SCF 6-31G*) and experimental [22] force constants for CF_4 along with the scale factor for each.

		Calculated (N m^{-1})	Experimental (N m^{-1})	Scale factor
$A_1(r)$	F_{11}	1127.5	923.5	0.819
$E(\alpha)$	F_{22}	83.5	70.5	0.844
$T_2(r)$	F_{33}	769.6	645.0	0.838
T_2	F_{34}	84.7	88.0	1.039
$T_2(\alpha)$	F_{44}	121.8	100.0	0.821

k_{rr} is an interaction constant for a pair of bonds;

$f'_{r\theta}$ is an interaction constant where the bond forms an arm of the angle;

$f''_{r\theta}$ is an interaction constant where the bond does not form an arm of the angle;

$f'_{\theta\theta}$ is an interaction constant between two angles which share a bond;

$f''_{\theta\theta}$ is an interaction constant between two angles which do not share a bond.

Only the following combinations of stretch–bend and bend–bend interactions can be determined [18]:

$$k_{r\theta} = (f'_{r\theta} - f''_{r\theta})\sqrt{2} \tag{1}$$

$$k'_\theta = f_\theta - f'_{\theta\theta} \tag{2}$$

$$k''_\theta = f_\theta - f''_{\theta\theta}. \tag{3}$$

These are related to the internal symmetry force constants of Guth and Hess [17] by:

$$k_r = \tfrac{1}{4}(F_{1,1} + 3F_{13,13}) \qquad k'_\theta = \tfrac{1}{2}(F_{5,5} + F_{14,14})$$

$$k_{rr} = \tfrac{1}{4}(F_{1,1} - F_{13,13}) \qquad k''_\theta = F_{14,14}. \tag{4}$$

$$k_{r\theta} = F_{13,14}$$

These valence force constants (table 1) were then used to calculate elastic moduli and phonon dispersion relations for diamond using the mathematical procedures outlined by [1].

Several authors [19–21] have shown that Hartree–Fock SCF calculations using double-zeta (split-valence) basis sets systematically give harmonic frequencies and force constants 10 to 30% larger than experimental values. For neopentane the average difference between calculated and measured molecular frequencies was 8.6% [17]. These errors can be attributed to inadequacies in the basis set, to neglect of electron correlation, and to anharmonicity in the experimental frequencies. In order to more easily compare calculated with experimental phonon dispersion curves for diamond, we have scaled our *ab initio* force constants for the neopentane C_5 cluster via parallel calculation for the isoelectronic molecule CF_4 for which reliable experimental force constants are available [22]. This avoids problems with uncertainties in the experimental force field for neopentane [17]. Scale factors were determined as the ratio of experimental to calculated (6-31G* basis set, RHF/SCF calculation) CF_4 internal symmetry force constants (table 2). These scale factors were then used to reduce the *ab initio* neopentane force constants. Both unscaled and scaled force fields used for the calculations on diamond are given in table 1.
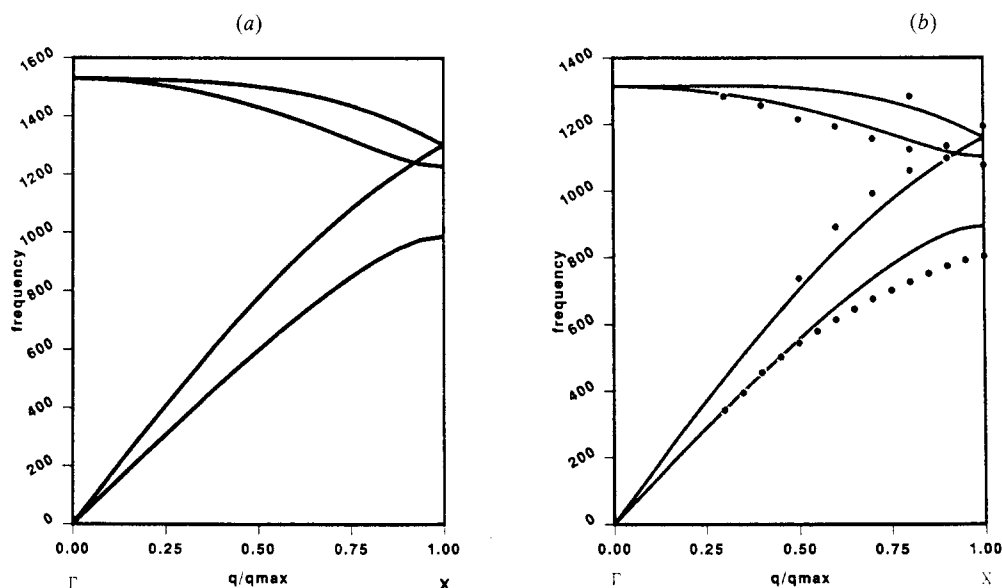
Figure 1. Diamond phonon dispersion relations in the [100] direction calculated from (a) as-calculated force constants and (b) scaled force constants; points are experimental data.

The C–C bond length, R, and associated lattice parameter, $a = 4R\sqrt{3}$, calculated from the molecule are 1.5351 and 3.5452 Å, respectively. These differ from the parameters obtained from x-ray measurements by 0.6%. The x-ray lattice parameter value of 3.5667 Å [23] has been used in our calculation of the elastic moduli.

3. Results

Our calculated dispersion curves are shown in figures 1, 2 and 3 for the directions [100] (Γ–X), [110] (Γ–K–X) and [111] (Γ–L), respectively. Figures 1(a), 2(a), and 3(a) were calculated using the unscaled force field and figures 1(b), 2(b) and 3(b) represent calculations using the scaled force field. Experimental phonon dispersion data [24, 25] are compared with our calculations in figures 1(b), 2(b) and 3(b). The calculated phonon dispersion curves using unscaled and scaled force constants are identical in topology. Experimental and calculated values of critical point frequencies are compared in table 3. The unscaled force constants give frequencies 10–23% larger than experiments, as expected from *ab initio* vibrational calculations for molecules [19]. Scaling reduces this error to less than 3%, except for the lowest frequency TA branches which are overestimated by 11%. In general, vibrational properties calculated using our scaled *ab initio* force constants are comparable in quality to those obtained in the pseudopotential calculation of Louie [11] (table 3), with less computational effort.

The calculated elastic moduli (C_{11}, C_{12} and C_{44}), bulk modulus ($K = \frac{1}{3}(C_{11} + 2C_{12})$) and shear modulus ($c' = \frac{1}{2}(C_{11} - C_{12})$) using both the scaled and unscaled force constants are given in table 4.

4. Discussion and summary

The most impressive feature of these results is that a very local, valence force field model was sufficient to calculate the significant vibrational characteristics of diamond
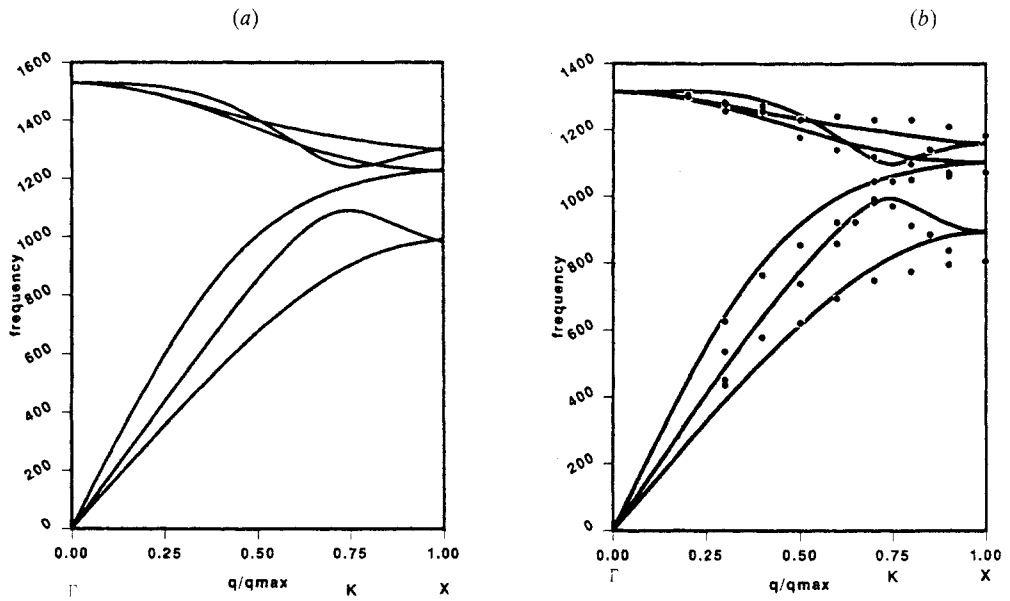
(a)

(b)

Figure 2. Diamond phonon dispersion relations in the [110] direction calculated from (a) as-calculated force constants and (b) scaled force constants; points are experimental data.

(a)

(b)

Figure 3. Diamond phonon dispersion relations in the [111] direction calculated from (a) as-calculated force constants and (b) scaled force constants; points are experimental data.
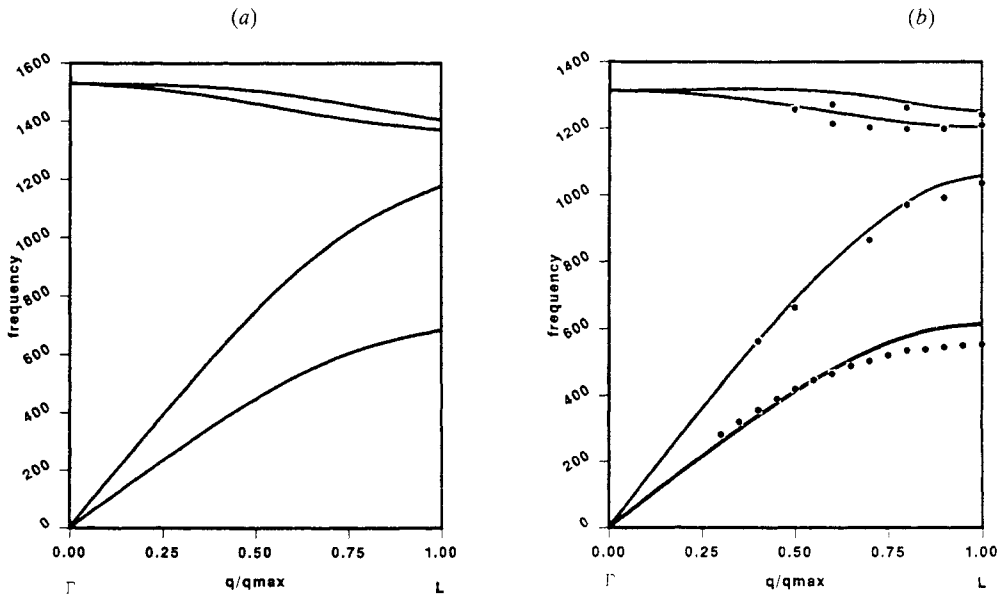
Table 3. Calculated critical point frequencies (in cm^{-1}) for diamond using the raw and scaled force constants. Experimental data from [11, 24, 25].

Mode	This work		Experimental [24, 25]	Pseudopotential [11]
	Unscaled	Scaled		
$\omega_{TO}(\Gamma) = \omega_{LO}(\Gamma)$	1529	1314	1333	1346.5
$\omega_{TO}(X)$	1227	1103	1077	1173.9
$\omega_{LO}(X) = \omega_{LA}(X)$	1301	1160	1194	1219.5
$\omega_{TA}(X)$	986	894	802	772.1
$\omega_{TO}(L)$	1375	1204	1209	—
$\omega_{LO}(L)$	1407	1251	1241	—
$\omega_{LA}(L)$	1160	1058	1034	—
$\omega_{TA}(L)$	674	614	552	—

Table 4. Calculated and experimental elastic moduli for diamond. In units of $(\times 10^{11}\,N\,m^{-2})$.

	This work		Experimental		Pseudopotential [11]
	Raw	Scaled	[26, 27]	[28]	
C_{11}	11.089	9.14	10.79	10.764	—
C_{12}	2.668	2.12	1.24	1.252	—
C_{44}	6.250	5.51	5.78	5.774	—
K	5.475	4.46	4.43	4.423	4.37
c'	4.210	3.51	4.72	4.756	—

to within good numerical agreement with experimental values. This may be said for even the unscaled force constants. However, as stated previously, the purpose of the scaling was to remove many of the inadequacies of the calculational model (i.e., basis set limitations and neglect of electron correlation). Presuming that this is the case, the remaining 3 to 11% error of the calculated phonon characteristics might be attributed to the neglect of longer range interactions.

One measure of the success of these calculations is the degree of agreement between calculated and experimental bulk moduli (0.7%). The bulk modulus represents homogeneous deformation of the diamond structure. In terms of the valence force constants, $K = (1/3a)(k_r + 6k_{rr})$ and involves no angle bending interaction terms [2]. Instead, it consists solely of bond-stretching-type interactions, k_r and k_{rr}. The excellent agreement with the experimental bulk modulus indicates that, at least, these interactions are well characterised by the model and that the combination of k_r and k_{rr} are quite sufficient for this description. The level of agreement is equivalent to that achieved by Louie [11] who used a more sophisticated pseudopotential model that includes non-local plane wave expansion of the electronic wave function.

With respect to the other calculated elastic moduli, their deviations from experiment appear to be associated with the angular dependent force constants. For instance, the shear modulus consists solely of angle bending terms where $c' = (6/a)(2k_\theta' - k_\theta'')$. Its underestimation by 25% accounts entirely for the underestimation of C_{11} (15%) and overestimation of C_{12} (71%). Consequently, modification of the valence force field for predicting elastic constants should focus on angle interaction terms.

Several authors have discussed the need and nature of longer range interactions for a successful fit to experimental phonon dispersion curves [3, 7, 8, 10]. In this study, the five force constants concern primarily the interactions of nearest neighbours of the central carbon atom in the C_5 structure. Tubino *et al* [7, 10] modelled the lattice dynamics of diamond with a valence force field similar to our own, but with an additional force constant, expressed as an interaction constant between two angles which share a bond but not a vertex. They, and McMurry *et al* [3] in an earlier publication, showed that omission of such force constants grew relatively less important in progressing from germanium to silicon and to diamond. Our results seem to indicate that this omission for diamond is fairly small in an absolute sense as well as with respect to the critical point frequencies. Nevertheless, inclusion of such a force constant can improve somewhat our estimations of phonon dispersion curves particularly for the TA modes at large wavevectors and our estimations of c' and the other elastic constants which contain bend–bend, bend–stretch terms. This may be accomplished by conducting similar cal-culations on somewhat larger molecules which allows for the determination of this parameter.

It is interesting to comment that even the additional force constants as proposed by Tubino and coworkers still reflects interactions on a very local scale. It in effect describes next nearest-neighbour interactions. This is as opposed to such forces as electrostatic interactions which may extend over many atomic distances. Our method of calculation is not capable from a practical point of view of including such interactions as Coulomb effects and it is clear that longer-range forces would be necessary for a more complete calculation. Nevertheless, it is encouraging in the case of diamond to find that con-siderable detail of the lattice dynamics of crystals can be obtained from very local, high-quality representations.

In summary, we have shown in the present study that given a reliable five-parameter valence force field determined for neopentane, it is possible to closely model the dynamical properties of diamond, as suggested by Musgrave and Pople [2]. Our cal-culated values agree very well with experiment in all cases except for the transverse acoustic modes near the zone edge and elastic constants which are defined most heavily in terms of angle bending type force constants, e.g., the shear modulus, c'. This work also demonstrates the utility of deriving valence force fields from *ab initio* calculations on suitable molecular clusters for non-empirical lattice dynamical calculations on con-densed phases [29].

Acknowledgments

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