Finite temperature electronic structure of Diamond and Silicon

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The electron-phonon interaction contribution to the electronic energies is included in density functional total energy calculations with \textit{ab initio} pseudopotentials via the formalism of Allen [Phys. Rev. B, 18 5217 (1978)] to obtain the temperature dependent electronic structure of diamond and silicon. This method allows us to obtain the thermally-averaged \textit{ab initio} electronic structure in a straightforward and computationally inexpensive way. Our investigations on the finite temperature electronic structure of diamond and silicon bring out that a new criterion, that of temperature transferability, is required in the input \textit{ab initio} pseudopotentials for temperature dependent studies. The temperature transferability of the Troullier-Martins pseudopotentials used in this work is strongly dependent on the cut-off radius and the inclusion of the unbound 3d state. The finite temperature indirect band gaps are highly sensitive to the choice of cut-off radius used in the pseudopotentials. The finite temperature band structures and density of states show that thermal vibrations affect the electron energies throughout the valence and conduction band. We compare our results on the band gap shifts with that due to the Debye-Waller term in the Allen-Heine theory and discuss the observed differences in the zero point and high temperature band gap shifts. Although, the electron energy shifts in the highest occupied valence band and lowest unoccupied conduction band enable to obtain the changes in the indirect and direct band gaps at finite temperatures, the shifts in other electronic levels with temperature enable investigations into the finite temperature valence charge distribution in the bonding region. Thus, we demonstrate that the Allen theory provides a simple and theoretically justified formalism to obtain finite temperature valence electron charge densities that go beyond the rigid pseudo-atom approximation.

I. INTRODUCTION

Most electronic structure studies are performed for static lattices that are implicitly assumed to be at 0 K. Experimental investigations and determination of material properties are however performed at finite temperatures. The two important effects of temperature on the material are the lattice expansion and lattice dynamics. The effect of the lattice expansion on electronic energies is straightforward to obtain. However, the electron-phonon interaction which has a major contribution from the lattice dynamical behaviour is harder to calculate. Temperature affects the nuclear motion in materials leading to lattice dynamics which alters the electronic energies by 2–4 $k_B T$ in solids. The resistivity of metals, directional Compton profiles, infrared, Raman, optical spectra, specific heats, heat conduction, band gaps etc. are affected by the electron-phonon interaction. In order to compare the results of experiments with the theoretical simulations the effect of electron-phonon interaction needs to be included in the calculations of these phenomena.

Although of significant importance, the electron-phonon interaction happens to be the most difficult to compute from first principles. Currently, there are three major approaches, namely, the molecular dynamics method, the frozen phonon method and the perturbation theory method to understand the effects of the electron-phonon interaction on material properties. Each of these approaches has its advantages and disadvantages. The to-date developments to include the electron-phonon interactions in \textit{ab initio} calculations and their computational implementations is discussed in detail in a rigorous and elegant review by Giustino.

In the context of temperature dependent semiconductor band gaps, the earliest attempt to include the electron-phonon interaction was by Fan, who calculated the self-energy (SE) contribution to the semiconductor band gap shifts. This term is also referred to as the Midgal term in superconductor literature. Soon afterwards, Antonić calculated the Debye-Waller (DW) correction to the semiconductor band gaps. Subsequently, several authors calculated the semiconductor band gap shifts due to thermal vibrations, mostly by incorporating the Debye-Waller term. These investigations led Baumann to suggest that both self-energy and DW corrections are necessary for a complete account of the role of thermal vibrations on electron energies.

Allen and Heine developed the formal basis for incorporating electron-phonon interactions in the harmonic approximation at constant volume using second-order perturbation theory. In this formalism, the DW term and the SE term appear separately and the total electron
energy shift is a sum of the two terms. The implementation of the formalism requires a concurrent calculation of the DW and SE term. The calculation of the DW term is approximated by a second order expansion with the neglect of the higher order terms. Further, by exploiting translational invariance the DW term (in the second order form) and the SE term is recast\textsuperscript{11} to have similar forms. All recent studies based on the Allen-Heine theory use the recasted DW term since calculating it directly in the second order form is computationally complex.

The Allen-Heine theory was earlier used with empirical pseudopotentials to obtain the band gap shifts in semiconductors\textsuperscript{11,15}. However, in the last decade, several \textit{ab initio} studies\textsuperscript{16–24} based on it have been reported. These studies report the band gap shifts at specific k points that usually correspond to the indirect and direct band gaps\textsuperscript{15,24}. In these studies, the band gaps at all high symmetry points or the complete valence electron band structure along the symmetry lines in the Brillouin zone have not been reported.

Subsequent to the Allen-Heine theory\textsuperscript{11}, a more accurate theory was developed by Allen\textsuperscript{2} for the temperature dependent band structure. In this theory, the DW term is considered to all orders instead of its truncated second order expansion as in the Allen-Heine theory. In the implementation of the Allen theory\textsuperscript{2} with pseudopotentials, the first step is to correct the pseudopotential form factor with the DW term and use this corrected pseudopotential to obtain the finite temperature electronic structure. The second step is to calculate the SE term using the wavefunctions and energies obtained from the DW corrected electronic structure.

The Allen theory\textsuperscript{2} provided the theoretical justification for the earlier empirical studies\textsuperscript{9,12} that calculated the finite temperature band gaps based on the DW correction step. It must be noted that the first step, the DW correction step, directly leads to the temperature dependent band structure. The band gap shifts obtained from the first DW correction step gave satisfactory band gap shifts in some cases and unsatisfactory results in other cases\textsuperscript{5,12}. The DW corrected empirical studies on the temperature dependence of band gaps in PbSe and PbTe, while giving reasonable results for the direct gap, failed to correctly estimate the indirect gap\textsuperscript{11}. Allen and Heine\textsuperscript{11} and Allen\textsuperscript{2} discuss this aspect and show that for accurate values of the finite temperature electron energies and band gap shifts the contribution from the SE term needs to be included, in general.

The second order Allen-Heine formalism\textsuperscript{2} continues to be of interest and has been used in several recent \textit{ab initio} calculation based studies\textsuperscript{19,22} to obtain the semiconductor band gap shifts with temperature. In contrast, the Allen theory\textsuperscript{2} has not been used in \textit{ab initio} studies, even though it is a more accurate approach\textsuperscript{11} compared to the Allen-Heine theory.

In this article we demonstrate that the Allen theory can be combined with \textit{ab initio} pseudopotentials to obtain \textit{ab initio} finite temperature electronic structures without any additional increase in the computational complexity of these calculations. We investigate the finite temperature electronic structure of diamond and silicon using the \textit{ab initio} pseudopotential implementation of the Allen theory. We then compare the results of our theoretical calculations with earlier \textit{ab initio} studies on diamond and silicon based on the second-order Allen-Heine theory.

The focus of this paper is to address the main issues that affect the implementation of the Allen theory\textsuperscript{2} using \textit{ab initio} pseudopotentials. Thus, only the DW contribution, which is the first step in Allen theory, has been calculated. The (Fan/Fan-Migdal) self-energy term, that is to be calculated from the results of the DW step, has not been evaluated.

However, calculation of the DW correction to the electronic energies is important for three reasons, as will be seen in this study. Firstly, the DW step is sufficient to address the fundamental question, viz. the viability of implementing Allen theory with \textit{ab initio} pseudopotentials. Secondly, only the DW term can be the basis for the comparison of the Allen and Allen-Heine theories. And, thirdly, the DW step is sufficient to obtain finite temperature valence electron charge densities. Thus, the results of the present study have important implications for \textit{ab initio} finite temperature electronic structure studies.

In the next section, we briefly describe the theory of Allen\textsuperscript{2} for the inclusion of the electron-phonon interaction and its implementation within the pseudopotential method for band structure calculations. In Sec. \textsuperscript{II} we describe the computational implementation and give the details of our calculations of temperature dependent electronic structure. Sec. [V] discusses the results of the temperature dependent band gap trends that were obtained using existing pseudopotentials and the need to use temperature transferable pseudopotentials in electronic structure calculations that are to be used to study the finite temperature properties. Our results on the temperature dependent band gap trends, band gap shifts at zero point vibration and higher temperatures for diamond (Sec. [IVB]) and silicon (Sec. [IVC]) are discussed in detail with implications. In the Sec. [IVE], we show that theoretically it is possible to obtain charge densities that go beyond the rigid pseudo-atom approximation for a direct comparison with experimental data and this is then followed by conclusions in Sec. [V].
\[ H_{e-p} = \sum_l [V(\mathbf{r} - \mathbf{R}_\alpha) - V(\mathbf{r} - \alpha)] \]  

where, \( V(\mathbf{r}) \) is the atomic potential, \( \mathbf{R}_\alpha \) is the displaced position of the atom, \( \alpha \) is the equilibrium position and \( \mathbf{u}_\alpha = \mathbf{R}_\alpha - \alpha \) is the displacement. The thermal displacements of atoms are time dependent and are related to the phonon frequency. The perturbed electron energy can be calculated in the adiabatic approximation by a second order Taylor expansion of Eq. 1 as proposed by Allen-Heine, where the first two terms are

\[ H_{e-p}^{(1)} = \sum_l \left[ \frac{\partial V(r - \alpha)}{\partial r_n} \right] u_{\alpha n} \]  

\[ H_{e-p}^{(2)} = \frac{1}{2} \sum_l \left[ \frac{\partial^2 V(r - \alpha)}{\partial r_n \partial r_m} \right] u_{\alpha n} u_{\alpha m} \]  

Considering the thermal average \( \langle H_{e-p} \rangle \), the only non-vanishing terms are the even powered terms like Eq. 3 in the Taylor expansion. The thermal average of Eq. 3 is the self-energy correction in a Bloch-wave basis set. However, in a plane wave basis set all the non-vanishing terms can be considered and result in the Debye-Waller corrections to the crystal potential and Eq. 4 can be rewritten as

\[ H_{e-p} = \sum_{kk'} V(k' - k)s(k' - k)c_k^\dagger c_{k'} \]  

In this equation the \( k, k' \) span all the Brillouin zones and \( s \) is the structure factor. The thermal average of the perturbed Hamiltonian in reciprocal space is

\[ \langle H_{e-p} \rangle = \sum_k \sum_{GG'} V(G' - G)(e^{-W(G' - G)} - 1)c_{k + G'}^\dagger c_{k + G} \]  

This Hamiltonian is periodic and the calculation in Fourier space requires the sum to be performed only on the first Brillouin zone. When added to the unperturbed Hamiltonian it leads to a reduction of the pseudopotential form factors \( V(G) \) of the static lattice by DW factors \( e^{-W(G)} \) to incorporate the effect of the DW term of the electron-phonon interaction. This result of Allen-Heine provided the theoretical basis for the earlier empirical studies and is also the theoretical basis for the present \textit{ab initio} study.

The underlying assumptions in both the Allen-Heine and Allen theories are the adiabatic approximation and the rigid atom approximation. The \textit{ab initio} pseudopotentials are generated under the assumption of frozen-core approximation for the core electrons, which satisfies the rigid-atom approximation. Thus, Allen-Heine and Allen theories are valid for semiconductors and insulators at all temperatures. The adiabatic approximation condition, however, breaks down for metals at low temperatures since the self-energy term cannot be correctly represented.

From Eq. 5 the finite temperature pseudopotential form factor for any ion can be written as

\[ V_{i}^{ps}(G, T) = V_{i}^{ps}(G, 0)e^{-W_{i}(G, T)} \]  

where the DW factor is given by, \( W_i = \langle u_i^2 \rangle |G|^2 \) and \( \langle u_i^2 \rangle \) is the mean square displacement of atom \( i \).

In order to use Eq. 6 in \textit{ab initio} studies, both the pseudopotential form factor, \( V(G) \) and the DW factor \( W \) need to be obtained from \textit{ab initio} studies. Currently, there are several \textit{ab initio} methods to calculate DW factor from first principles. In these studies, \textit{ab initio} DW factor has already been calculated for several materials including many semiconductors.

However, if necessary, even experimental DWF can be used in Eq. 6. We note that in several \textit{ab initio} studies experimental lattice parameters are used. In particular, Erba et. al provide the justification for the use of experimental lattice parameters viz. that they can be validated by separate \textit{ab initio} studies. Therefore, if necessary, the same justification can be the basis for the use of experimental DWF in \textit{ab initio} studies based on Allen theory.

The other requirement is that of \textit{ab initio} pseudopotentials which can be used in Eq. 6 to obtain finite temperature band structure. As discussed in Sec IV this is a much more stringent condition than expected.

It is of interest to compare both the zero-point and the higher temperature band gap shifts obtained using the Allen and Allen-Heine theories since the latter use the second-order approximation to the DW term. In both, Allen and Allen-Heine theories, the band gap shifts should increase with temperature due to the increase in the mean-square displacements or \( W \). The main difference in their formalism is that, in the Allen-Heine theory, the pseudopotential form factor \( V_G e^{-W(G)} \) is approximated by \( V_G (1-W) \) neglecting higher order terms in the expansion. The band gaps obtained by the DW corrected pseudopotentials, \( V_G e^{-W} \) in the Allen theory and \( V_G (1-W) \) in the Allen-Heine theory, are to be compared with the band gaps obtained with the static lattice pseudopotential form factor, \( V_G \), to obtain the finite temperature band gap shifts.

We can examine the effect of the second-order approximation used in the Allen-Heine theory. For higher values of the mean square displacement, the pseudopotential form factor in the Allen-Heine theory, \( V_G (1-W) \), is smaller than that of the actual value, \( V_G e^{-W} \), that is used in the Allen theory. This implies that the pseudopotential form factor used in the Allen-Heine theory undergoes a larger amount of change from the static lattice value \( V_G \) than the pseudopotential form factor in the Allen theory. It follows that, at higher temperatures, the Allen-Heine theory should give larger band
gaps shifts than Allen theory due to the neglect of higher order terms.

In the Allen-Heine theory, the self-energy (SE) term contribution is calculated from the static lattice electron wavefunctions and energies. In contrast, in the Allen theory, the SE term contribution is to be calculated from the finite temperature electron wavefunctions and energies obtained from the DW correction step. Thus, the SE term contributions in the Allen and the Allen-Heine theories will be different.

Therefore, the primary basis for the comparison of the Allen-Heine and Allen theories is the Debye-Waller (DW) term contribution, which, in principle, must give identical band gap shifts for the same pseudopotential and same mean-square displacement values as long as the second-order approximation is valid.

### III. COMPUTATIONAL METHODOLOGY

We have performed ab initio total energy calculations based on density functional theory to obtain the band structure of diamond and silicon at different temperatures using the Quantum Espresso (QE) software package. The equilibrium lattice constant for the static lattice (0 K) was obtained by choosing the energy converged k-point mesh and kinetic energy cutoff. A 6x6x6 k-point mesh and kinetic energy cutoff of 60 Ry for carbon (diamond) and 40 Ry for silicon was used in all our calculations.

To incorporate the effect of finite temperature on the electronic structure, we modified the QE code so that the local part of the ab initio atomic pseudopotential of the system under investigation is altered in G-space with the Debye-Waller factor, i.e. $e^{-W}$ as in Eq. 4. The non-local part of the atomic pseudopotential is unmodified to preserve the angular dependence of the scattering potential as in the earlier work based on empirical pseudopotentials. With this alteration, the finite temperature pseudopotential form factor is obtained within the QE code for a given ab initio static lattice pseudopotential of any atom. Using a value of the mean square displacement $\langle u_i^2 \rangle$ appropriate for a chosen temperature, an electronic structure calculation was performed to obtain the band structure at that temperature.

All electronic structure calculations were performed for various temperatures up to 1000 K at constant volume using the equilibrium lattice constant obtained for the static lattice. The ab initio mean-square displacement $\langle u_i^2 \rangle$ values of C and Si listed in Table I at various temperatures were taken from the ab initio studies of Schowalter et al. Using these values in the modified QE code, the self-consistent total energy and the band structure at different temperatures were obtained using different kinds of ab initio pseudopotentials.

| T (K) | $\langle u_i^2 \rangle$ (Å²) |
|-------|-----------------------------|
|       | C                            | Si               |
| 0.001 | 0.001611                    | 0.002471         |
| 100   | 0.001626                    | 0.003196         |
| 200   | 0.001699                    | 0.004865         |
| 300   | 0.001807                    | 0.006788         |
| 400   | 0.001968                    | 0.008772         |
| 600   | 0.002436                    | 0.01287          |
| 800   | 0.002962                    | 0.017022         |
| 1000  | 0.003529                    | 0.021198         |

**TABLE I**: Ab initio mean-square displacement values for diamond and silicon at various temperatures.

### IV. RESULTS AND DISCUSSION

We began our investigations on the effect of temperature on the electronic structure of diamond and silicon with several norm conserving pseudopotentials that are available in the pseudopotential library on the QE website. In addition, some optimized and ultrasoft pseudopotentials available on the QE website library, recently developed Optimized Norm Conserving Vanderbilt (ONCV) pseudopotentials, the GBRV, empirical pseudopotentials, and PAW pseudopotentials were also investigated.

Separate electronic structure calculations were performed to obtain the band structure of diamond and silicon for each temperature up to 1000 K as given in Table II, using each pseudopotential listed in Table I and III. The band gaps obtained for each pseudopotential were then compared across the range of temperatures used in this study. Table II and III list the trends in the band gaps obtained for diamond and silicon from our calculations. The equilibrium lattice parameter obtained for each pseudopotential is listed along with the experimental value for comparison.

For the static lattice case, almost all of the above pseudopotentials show excellent agreement in values of the indirect and direct band gaps reported in theoretical studies as all these pseudopotentials have hitherto been developed for static lattice ab initio calculations.

Several previous studies on diamond and silicon, based on the Allen-Heine theory, using both ab initio and empirical pseudopotentials, have shown that the indirect and direct band gaps decrease with temperature in agreement with experiments. In particular, for diamond and silicon, the DW term alone leads to a decrease in the band gaps with temperature as calculated in the Allen-Heine theory.

Thus, the primary criterion that needs to be fulfilled when choosing ab initio pseudopotentials for temperature dependent studies on carbon (diamond) and silicon is that after modification with the DW factor, the direct and indirect band gaps must decrease with increasing temperatures. Only after this primary criteria is met.
ab initio calculations show a decrease in the indirect band gap and an increase in the direct band gap with increasing temperature. However, the direct band gaps observed for the above pseudopotentials are in general increasing with temperature. This is expected as the ab initio calculations are performed for static lattice conditions. It is well known that the Si band gaps are underestimated in the density functional calculations. A consequence of this underestimation is that at higher temperatures of 800 K and 1000 K the indirect band gap of Si is seen to vanish. As will be discussed in detail later (Section IV C), while the band gap trends are correct, the actual values of the band gap shifts for the above pseudopotentials, Si_{pbe-gipaw}, appear to be excessive when compared to literature values.

The finite temperature band gap results show that, in general, the ab initio pseudopotential developed for static lattice applications cannot be directly used for temperature dependent electronic structure calculations. The above results thus imply that for finite temperature studies, ab initio pseudopotentials need to be generated so as to satisfy an additional criterion, that of temperature transferability. Since the ab initio pseudopotential is initially generated for static lattice conditions, it has to be generated with the usual criteria viz. the norm conservation criteria (present or absent) and the choice of the cut-off radius, r_c, to ensure the transferability of the pseudopotential to other chemical environments. The additional criterion of temperature transferability will ensure that the pseudopotentials can be used for finite temperature studies, in addition to static lattice calculations.

Semiconductors are the class of materials that are most suited to test for temperature transferability. This is because there is a stringent test of temperature transferability - the indirect and direct band gaps must exhibit the “Varshni effect” of redshift with increasing temperature. In addition, the band gap shifts must
be of the same order of magnitude when compared with existing experimental or theoretical results.

However, in some semiconductors the band gaps exhibit a blusshift with temperature. For such semiconductors, the temperature transferability criterion stands appropriately modified.

### A. Pseudopotentials with temperature transferability

Considering that several of the currently available open source C and Si ab initio pseudopotentials (Table II and III) when used for finite temperature electronic structure calculations did not reproduce the correct band gap trends and band gap shifts, we generated pseudopotentials based on the Troullier-Martins method\(^\text{[10]}\), with GGA/PBE\(^\text{[11]}\) and LDA/PZ\(^\text{[12,13]}\) exchange-correlation functionals, using the OPIUM\(^\text{[14]}\) pseudopotential generation code.

Table V and VI list the details of the carbon and silicon pseudopotentials (PP) that were generated and tested for temperature transferability. The cut-off radius, the number of valence states and their electron occupancies were varied to study their effect on temperature dependent band gap behavior and to identify pseudopotentials that exhibit temperature transferability.

![Graph showing band gap shift vs. cut-off radius for diamond](image)

**FIG. 1:** Variation of zero-point band-gap shifts with cut-off radius for diamond

| PP Name | Valence electrons | \(r_c\) (a.u.) | \(E_x\) | Finite T trend | Indirect | Direct |
|---------|------------------|----------------|-------|---------------|---------|--------|
| C\(_1\) | \(2s^2 2p^2\)   | 1.5            | PBE   | Decrease Decrease |
| C\(_2\) | \(2s^2 2p^{1.5}\) | 1.5            | PBE   | Decrease Decrease |
| C\(_3\) | \(2s^2 2p^1\)   | 1.5            | PBE   | Decrease Decrease |
| C\(_4\) | \(2s^2 2p^2\)   | 1.5            | PZ    | Decrease Decrease |
| C\(_5\) | \(2s^2 2p^2\)   | 1.2            | PBE   | Increase Decrease |
| C\(_6\) | \(2s^2 2p^{1.5}\) | 1.2            | PBE   | Increase Decrease |
| C\(_7\) | \(2s^2 2p^1\)   | 1.2            | PBE   | Increase Decrease |
| C\(_8\) | \(2s^2 2p^2 3d^0\) | 1.5          | PBE   | Decrease Decrease |
| C\(_9\) | \(2s^2 2p^{1.5} 3d^0\) | 1.5        | PBE   | Decrease Decrease |
| C\(_10\)| \(2s^2 2p^1 3d^0\) | 1.5            | PBE   | Decrease Decrease |
| C\(_11\)| \(2s^2 2p^2 3d^0\) | 1.5            | PZ    | Decrease Decrease |
| C\(_12\)| \(2s^2 2p^2 3d^0\) | 1.3            | PBE   | Inc-Dec Decrease |
| C\(_13\)| \(2s^2 2p^2 3d^0\) | 1.4            | PBE   | Inc-Dec Decrease |
| C\(_14\)| \(2s^2 2p^2 3d^0\) | 1.6            | PBE   | Decrease Decrease |
| C\(_15\)| \(2s^2 2p^2 3d^0\) | 1.7            | PBE   | Decrease Decrease |

**TABLE V:** The trend in the indirect and direct band gap values with temperature increased up to 1000 K for the different carbon (diamond) Troullier-Martins ab initio pseudopotentials generated with PBE and PZ exchange correlation functional to study finite temperature behavior.

From Table V, the pseudopotentials C\(_1\) – C\(_4\) and C\(_8\) – C\(_{11}\) generated with a \(r_c\) of 1.5 a.u. showed the expected trend of decreasing direct and indirect band gaps with increasing temperature. However, the band gap shifts in the two sets, C\(_1\) – C\(_4\) and C\(_8\) – C\(_{11}\), differ by about 4-7 meV. We note that the pseudopotentials C\(_5\) – C\(_7\), that differ from C\(_1\) – C\(_3\) only in the cut-off radius, are not temperature transferable highlighting the sensitivity to this parameter.

To further examine the sensitivity to the cut-off radius, pseudopotentials, C\(_{12}\) - C\(_{15}\) were generated with cut-off radius varying from 1.3 to 1.7 a.u. From Table V it is seen that the correct trends are seen only for cut-off radius of 1.5 a.u. and above. Figure I plots the variation of the zero-point indirect and direct band gap shifts as a function of the cut-off radius for the carbon pseudopotentials, generated in the \(2s^2 2p^2 3d^0\) configuration with the PBE exchange-correlation functional.

The zero-point direct band gap shift decreases weakly with the cut-off radius. This is an important result for comparison of the Allen and the Allen-Heine theories as discussed in Sec. IV B. In contrast, the indirect zero-point band gap shift varies strongly with the cut-off radius. The zero-point band gap shift is positive for \(r_c\) < 1.5 a.u. leading to an increase in the indirect band gap. Hence, carbon pseudopotentials with \(r_c\) < 1.5 a.u. do not exhibit temperature transferability. Only carbon pseudopotentials with \(r_c\) > 1.5 a.u. exhibit temperature transferability.

For silicon, from Table VI, pseudopotentials Si\(_8\) – Si\(_{10}\), Si\(_{pbe-giapaw}\) and Si\(_{12}\) – Si\(_{16}\) give the correct band gap trend with temperature. The pseudopotentials Si\(_1\) - Si\(_4\) have the same cut-off radius (1.7 a.u.) but different valence states and their occupancies. These pseudopotentials give only the zero-point indirect band gap to be larger than that of the static lattice. For all other temperatures, the indirect band gaps decrease with increasing temperature and are smaller than that of the static lattice. In the case of the direct band gap, the zero-point band gaps are larger.
than that of the static lattice. For all other temperatures, the direct band gaps decrease in comparison with the zero-point vibration gap but are higher than that of the static lattice up to temperature of 800 K.

| PP Name | Valence electrons | \( r_c \) (a.u.) | \( E_{xc} \) | Finite T trend |
|---------|------------------|-----------------|--------------|---------------|
| Si_1    | 3s^2 3p^2        | 1.7             | PBE          | Inc-Dec       |
| Si_2    | 3s^2 3p^{1.5}    | 1.7             | PBE          | Inc-Dec       |
| Si_3    | 3s^2 3p^1        | 1.7             | PBE          | Inc-Dec       |
| Si_4    | 3s^2 3p^2 3d^0   | 1.7             | PBE          | Inc-Dec       |
| Si_5    | 3s^2 3p^2        | 2.0             | PBE          | Decrease      |
| Si_6    | 3s^2 3p^{1.5}    | 2.0             | PBE          | Decrease      |
| Si_7    | 3s^2 3p^1        | 2.0             | PBE          | Decrease      |
| Si_8    | 3s^2 3p^2 3d^0   | 2.0             | PBE          | Decrease      |
| Si_9    | 3s^2 3p^{1.5} 3d^0 | 2.0        | PBE          | Decrease      |
| Si_10   | 3s^2 3p^1 3d^0   | 2.0             | PBE          | Decrease      |
| Si_{pbe-gipaw} | 3s^2 3p^1 3d^0 | 2.2             | PBE          | Decrease      |
| Si_12   | 3s^2 3p^1 3d^0   | 2.2             | PBE          | Decrease      |
| Si_13   | 3s^2 3p^2 3d^0   | 1.8             | PBE          | Decrease      |
| Si_14   | 3s^2 3p^2 3d^0   | 1.9             | PBE          | Decrease      |
| Si_15   | 3s^2 3p^2 3d^0   | 1.9             | PBE          | Decrease      |
| Si_16   | 3s^2 3p^2 3d^0   | 1.9             | PBE          | Decrease      |

TABLE VI: The trend in the indirect and direct band gap values with temperature increased up to 1000 K for the different silicon Troullier-Martins \textit{ab initio} pseudopotentials generated with PBE exchange correlation functional to study finite temperature behavior.

For the pseudopotentials Si_5-Si_7, that were generated with a cutoff radius of 2.0 a.u., the zero-point indirect band gap shows the correct behaviour i.e. smaller than the indirect band gap of the static lattice. The trend in the direct band gaps however is the same as that of Si_7 pseudopotentials up to a temperature of 600 K. Thus, the pseudopotentials Si_1-Si_7 do not exhibit temperature transferability.

Table VII shows that the pseudopotentials Si_8-Si_10 differ from pseudopotentials Si_5-Si_7 in that the unbound 3d^0 state was incorporated in the generation condition. These pseudopotentials show the correct indirect and direct band gap behavior and are hence, temperature transferable. This leads to the conclusion that incorporation of the unbound 3d^0 state in the pseudopotential generation configuration is essential for temperature transferability of Si pseudopotentials. In addition, the pseudopotential Si_12 was generated with the same conditions as Si_{pbe-gipaw} except that it did not have the gipaw construction. Both Si_12 and Si_{pbe-gipaw} (Table IV) give virtually identical indirect and direct band gap shifts at all temperatures. This suggests that the gipaw construction does not affect temperature transferability.

To examine the dependence of the band gap shifts on the cut-off radius, pseudopotentials Si_13 - Si_16 were generated in the 3s^2 3p^2 3d^0 configuration with the cut-off radius varying from 1.8 a.u to 2.2 a.u. Figure 2 plots the zero-point indirect and direct band gap shifts as a function of the cut-off radius. It is again seen that the zero-point indirect band gap shift varies strongly with the cut-off radius. In comparison, the zero-point direct band gap shift varies much more slowly with the cut-off radius.

To summarize, the temperature transferability of Troullier-Martins pseudopotentials is dependent on the choice of the cut-off radius and the inclusion/exclusion of the unbound 3d^0 state in the generation configuration. The cut-off radius strongly affects the indirect band gap.

These observations in combination with the usual criteria for pseudopotential generation indicate that only in a small subset of the generation parameter space of Troullier-Martins pseudopotentials the new criterion of temperature transferability is also satisfied. These observations will also be helpful in generating temperature transferable pseudopotentials for other elements that are constituents of compound semiconductors.

The question of whether other category of pseudopotentials, Optimized, Ultrasoft and ONCV pseudopotentials can also be generated to exhibit temperature transferability needs to be explored.

B. Finite temperature band structure - Diamond

We calculated the finite temperature electronic structure of diamond (a wide band gap material) at various temperatures listed in Table I from 0 – 1000 K by using the DW corrected pseudopotential form factors. While the calculations were performed for all the pseudopotentials listed in Table IV, we discuss here the results obtained for pseudopotentials that exhibit the correct band gap trends.
The zero-point band gap shifts fall into two clear sets for C_8-C_11 where the former gives slightly higher shifts of 4-7 meV. All these pseudopotentials have the same cut-off radius (1.5 a.u.).

The main difference between the two sets is the incorporation of the unbound 3d^0 state in the pseudopotential generation configuration in C_8-C_11. Thus, for the case of diamond, the incorporation of the unbound 3d^0 state in the generation configuration has a consistent, but minor, effect.

The pseudopotentials C_14 and C_15 vary from C_8 only in the cut-off radius. The choice of the cut-off radius strongly influences the indirect zero-point band gap shifts. The direct zero-point band gap shifts vary weakly with the cut-off radius. Comparing with the previous results based on the Allen-Heine theory, for the direct and indirect band gap shifts due to the DW term, the pseudopotentials we generated with the cut-off radius of 1.5 a.u. give the closest agreement. Hence, we restrict our discussion to the results obtained with C_8 and C_11 pseudopotentials that differ in the generation parameters only in the exchange-correlation functional.

For diamond, the lattice constants and the static lattice band gaps are very similar to that in previous ab initio studies. The band gaps are lower than the experimental values due to the well known underestimation of band gaps in density functional theory.

From Table VII it is seen that the lattice parameters for pseudopotentials with the LDA(PZ) parameterization (C_4 and C_11) are lower than others with the GGA(PBE) parameterization. In addition, the zero-point band gap shifts for pseudopotentials with the LDA(PZ) parameterization C_4 and C_11 (Table VII) are higher than others with the GGA(PBE) parameterization. Both these trends are similar to results from previous studies. In particular, the lattice parameter for the pseudopotential C_11 is 6.64 a.u. and is very similar to 3.52 Å and 6.652 Bohr for the pseudopotential with the same generation conditions. In addition, the direct band gap for the pseudopotential C_11 is 5.68 eV that is very close to the value of 5.67 eV for the similar ‘reference’ pseudopotential in Ponce et al. The similarities on the lattice parameter and band gap for the pseudopotential C_11 with earlier results justifies further comparisons.

Figure 3 plots the static lattice (0 K) band structure of diamond and also the thermally-averaged band structures (at 300 K and 1000 K) for the pseudopotential C_8 for in the vicinity of the Fermi level. The band structure is plotted so that the Fermi level at each temperature is at 0 eV. Fig. 3 demonstrates that the finite temperature thermally-averaged band structure can be obtained via an ab initio electronic structure calculation using ab initio pseudopotentials using the Allen theory formalism. The finite temperature band structures show that the valence and conduction bands shift by different amounts for different k points. From Fig. 3, it is clear that the temperature dependent band gap shifts can be obtained for any k point.

![Graph of band structure](image)

### Table VII: The lattice constant, indirect and direct band gaps for the static lattice and zero-point energy shifts in the direct and indirect band gaps for diamond obtained from temperature transferable pseudopotentials

| PP Name | Static lattice (a.u.) | Indirect Zero point shift (eV) | Direct Zero point shift (meV) |
|---------|----------------------|-------------------------------|-------------------------------|
| C_1     | 6.74                 | 4.26                          | 5.634                         | 102                           | 140                           |
| C_2     | 6.73                 | 4.28                          | 5.635                         | 102                           | 142                           |
| C_3     | 6.71                 | 4.33                          | 5.66                          | 103                           | 147                           |
| C_4     | 6.66                 | 4.31                          | 5.68                          | 107                           | 149                           |
| C_8     | 6.72                 | 4.215                         | 5.62                          | 96                            | 135                           |
| C_9     | 6.71                 | 4.247                         | 5.64                          | 96                            | 138                           |
| C_10    | 6.70                 | 4.29                          | 5.654                         | 95                            | 141                           |
| C_11    | 6.64                 | 4.27                          | 5.68                          | 100                           | 143                           |
| C_14    | 6.70                 | 4.25                          | 5.65                          | 165                           | 140                           |
| C_15    | 6.68                 | 4.29                          | 5.67                          | 205                           | 146                           |
To understand the effect of temperature on the complete band structure we plot the density of states (DOS) for the carbon pseudopotential C\textsubscript{8} at 0 K and 300 K in Figure 4. The effect of temperature on the valence electron energy diagram is noticeable from the change in the DOS at 300 K. The DW term causes a positive shift of the valence electron energy levels towards the Fermi energy. The unfilled conduction band energy levels on the other hand experience a negative shift towards the Fermi energy. This feature is observed in the DOS of all finite temperature band structures that we have calculated. In the filled as well as unfilled electron energy levels, the amount of shift experienced from the static lattice is different for different levels indicating that the levels are not just scaled uniformly by a temperature dependent scaling constant.

Figure 5 plots the indirect and direct band gap shifts of diamond due to the DW term for the four carbon pseudopotentials, C\textsubscript{8}-C\textsubscript{11}, at various temperatures. The indirect and direct band gap shifts show a non-linear behavior at low temperatures and a linear behavior at higher temperatures consistent with experimental observations\textsuperscript{22}. While we have calculated the shifts for all pseudopotentials at all temperatures under investigation, we plot the results only for the pseudopotentials that exhibit good temperature transferability behavior and hence are of interest for further studies. We note that the indirect band gap shifts decrease more rapidly with temperature than the direct band gap shifts and the changes in the generation configuration, in terms of the occupancies of the 2p state, has only a minor effect at all temperatures.

1. Zero-point band gap shifts

Zero-point vibrations represent the minimum perturbation to the static lattice system. Hence, it is of interest to examine the zero point band gap shifts in detail. For zero-point shifts, we assume that the DW term can be approximated by the second order expansion and the neglect of higher order terms in Allen-Heine theory is unimportant. That is, $V_G e^{-W} \approx V_G (1-W)$ and the Allen and Allen-Heine theories should give similar zero-point band gap shifts.

Of the several \textit{ab initio} studies\textsuperscript{17-24} on the band gap shifts in diamond based on Allen-Heine theory, only two\textsuperscript{17,18} give separately the contributions of the DW and the SE terms. Hence, the DW contribution to the zero-point shifts in our study (Table VII) can be compared with only these studies\textsuperscript{17,18}. In particular, our C\textsubscript{11} pseudopotential has the same generation conditions as the pseudopotential in Giustino et al.\textsuperscript{17} and the ‘reference’ pseudopotential in Ponce et al.\textsuperscript{18}. These studies, however, report the DW contribution only to the direct band gap and hence, the comparison is restricted to it.

The DW contribution to the direct band gap shifts for the pseudopotentials in the present study range from 135-149 meV for a variety of pseudopotential generation conditions (Table VII). In contrast, the indirect band gap shifts of these pseudopotentials (Table VII) have a much wider spread (95-205 meV) on account of the sensitivity to cut-off radius. For the direct as well as indirect band gap shifts, the pseudopotentials generated with PBE exchange correlation functional and that include the 3d\textsuperscript{0} state give comparatively lower shifts for a constant cut-off radius. When the direct band gap shifts are compared to the literature values\textsuperscript{17,18} of 105-121 meV for the zero-point shifts in the Allen-Heine theory, for Troullier-Martins pseudopotentials with a variety of generation conditions, our results are higher by about 20-30 meV.

In particular, Giustino et al.\textsuperscript{17} report a zero-point shift of 117 meV (19\% of 615 meV) due to the DW term for
the direct band gap of diamond. Poncé et al. report that the DW contribution ranges from 105-121 meV for four (Troullier-Martins) pseudopotentials. Of these, they report a direct band gap shift of 115 meV for the reference pseudopotential, with the same generation conditions as in Giustino et al. and in C11 in the present study. This is virtually identical to the DW zero-point shift of 117 meV reported in Giustino et al. Thus, the differences in the total (DW+SE) zero-point shifts to the fact that the SE contribution. The DW contribution to the zero-point direct band gap shift for the C11 pseudopotential in the present study is 143 meV. This value can be directly compared and is ~26 meV higher than that reported in the above studies.

2. Finite temperature band gap shifts

The DW contribution to the band gap shifts calculated in the present study can also be compared with results from Allen-Heine theory at high temperatures, where the higher order terms may become important. We compare the DW contribution to the direct band gap shifts obtained with the C11 pseudopotential since it has the same generation configuration as in literature.

Our calculated DW band gap shift of 152 meV at 200 K, 164 meV at 300 K and 231 meV at 600 K compares well with the reported DW contribution to the direct band gap shift of ~160 meV at 200 K, 190 meV at 300 K and 280 meV at 600K in literature. However, an inversion must be noted. Our finite temperature DW band gap shifts are smaller while our zero-point shifts are larger compared to literature values.

As seen in the previous section, there is a difference of ~26 meV between the results obtained using the Allen and Allen-Heine theory in the DW zero-point band gap shifts. Further insight can be gained if the differences are compared with respect to the zero-point shifts which eliminates the effect of the different zero-point band gap shifts. This helps to examine the increase in the band gap shifts due to the increase in the mean-square displacements with temperature.

Eliminating the zero-point shifts, the additional DW band gap shift in our study is 9 meV at 200 K, 21 meV at 300 K and 87 meV at 600 K. These small increases in the band gap shifts with temperature can be attributed to the fact that the \( u_i^2 \) changes very slowly with temperature for diamond. For example, \( u_i^2 \) varies from 0.00161 Å\(^2\) (0.001 K) to 0.00169 Å\(^2\) (200 K) to 0.0018 Å\(^2\) (300 K) at low temperatures.

In comparison, in Giustino et al., after eliminating the zero-point shifts, the additional DW band gap shifts are ~40 meV at 200 K, 70 meV at 300 K and 160 meV at 600 K. Compared to our results above, the relatively large band gap shifts for very small increases in the mean-square displacement values (especially upto 300 K) appear excessive.

C. Silicon

Silicon, a small band gap semiconductor used extensively in a wide range of technology applications is well studied experimentally as well as theoretically and is of interest for its temperature dependent properties. We calculated the finite temperature thermally-averaged electronic structure of silicon at various temperatures listed in Table VIII by using the DW factor modified pseudopotential. We performed the finite temperature calculations for all pseudopotentials listed in Table VII.

Table VIII lists the zero-point shifts in the indirect and direct band gap for all the temperature transferable pseudopotentials. It shows that pseudopotentials Si_{pbe-gipaw}, which differ only in the valence state occupancies of \( p \) electrons, have similar zero-point shifts. The band gap shifts are virtually identical for Si_{pbe-gipaw} (Table IV) and Si_{12} not only for zero-point vibrations but also for all other temperatures in our study. The band gap shifts increase monotonically for Si_{13} - Si_{16} indicating a strong dependence on the cut-off radius as seen in Figure 2.

| PP          | a (\( \text{amu} \)) | Band gap (eV) | Indirect | Direct |
|-------------|----------------------|----------------|----------|--------|
| Si_{11}     | 10.33                | 2.565          | 63.1     | 20.7   |
| Si_{12}     | 10.33                | 2.567          | 65.3     | 21     |
| Si_{13}     | 10.34                | 2.565          | 23       | 11     |
| Si_{14}     | 10.33                | 2.565          | 50       | 18     |
| Si_{15}     | 10.32                | 2.566          | 79       | 24.6   |
| Si_{16}     | 10.31                | 2.566          | 91       | 27     |

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| Si_{15}     | 10.32                | 2.566          | 79       | 24.6   |
| Si_{16}     | 10.31                | 2.566          | 91       | 27     |

TABLE VIII: The lattice constant, indirect and direct band gaps for the static lattice and zero-point direct and indirect band gap shifts for silicon obtained from temperature transferable pseudopotentials.

The static lattice direct (2.56 eV) and indirect (0.63 eV) band gaps for these pseudopotentials are very close to literature values of 2.55 eV and 0.62 eV respectively. Si_{12}, Si_{pbe-gipaw}, Si_{16} with higher cut-off radius have higher indirect band gap shifts and Si_{13}, Si_{14} with a lower cut-off radius have lower band gap shifts. As observed in diamond, the indirect band gap shifts are highly sensitive to the cut-off radius used in the pseudopotentials.

Previous literature values for the total (DW + SE) shift of the indirect band gap due to zero-point vibrations are 57 meV, 60 meV and 64.3 meV and the experimental values are 62-64 meV. For the direct band gap, the reported values are 22 meV and 47 meV and the experimental values are 25±7 meV.

Previous studies, though based on empirical pseudopotentials, suggest that in silicon the DW term overes-
FIG. 6: The direct (D) and indirect (I) band gap shifts in silicon due to the DW term with increasing temperature for different temperature transferable pseudopotentials.

FIG. 7: The calculated band structure (static lattice and thermally-averaged) of silicon at 0K, 300K and 600K in the vicinity of the Fermi level. The violet line represents the band structure at 0 K, the blue line at 300K and the red line at 600 K.
based on the Allen-Heine theory. The mean square displacement values as in previous studies however, could not be used since they have not been reported.

The implementation of Allen theory is based on using explicit values of the mean-square displacements, whereas in the Allen-Heine theory the mean-square displacement values are not directly used and are implicit. In our study of finite temperature properties of diamond and silicon explicit values of the mean-square displacements obtained from ab initio studies have been used. If the values of the mean-square displacements are different from that in the earlier studies, then discrepancies can be expected in the results from the two theories.

In the case of diamond, we have used (Table 1) the zero-point mean-square displacement values reported in Schowalter et al. A similar value, for the zero-point vibrations, has also been reported in Yang et al. In both these studies the mean-square displacement values have been obtained from density-functional perturbation theory. The previous Allen-Heine based study that reported the DW contribution to the direct band gap shift also use the density-functional perturbation theory to account for thermal vibrations, though explicit values of the zero-point mean-square displacements are not reported. Since there are some discrepancies in the DW band gap shifts for diamond (as seen earlier), it would be of interest to compare the zero-point mean-square displacements implicit in the Allen-Heine theory based studies with the explicit values reported in literature that are used in our study based on the Allen theory.

If the mean-square displacement values used in the two theories are the same, then the discrepancies, if any, are likely due to the different numerical implementations of the electron-phonon contribution to the electronic energies in the two theories.

Clearly, further studies are needed to fully understand the results obtained using the Allen and Allen-Heine theories. Such studies for any semiconductor, however, must necessarily use temperature transferable pseudopotentials.

E. Finite temperature valence charge density

Finite temperature charge densities are of interest, both theoretically and experimentally, to study bonding in materials. At present, there is no simple ab initio method to obtain finite temperature valence electron wavefunctions or charge densities. Currently, finite temperature charge densities are obtained from static lattice calculations with empirical approaches to incorporate the effect of thermal vibrations as discussed below.

The valence electron densities have been experimentally obtained for several materials from x-ray diffraction and electron diffraction studies. In particular, silicon and diamond are considered to be the prototype materials in experimental (valence) electron density studies. In these studies, the ‘fundamental step’ is to correct for the observed intensities at finite temperatures with the DW factor. Following this correction, an effective static lattice charge density is obtained. Subsequently, these charge densities are compared with theoretical ab initio calculations performed for static lattice.

Alternately, the theoretical charge density from static lattice calculations are altered by incorporating thermal vibrations through the DW factors and the finite temperature charge densities or structure factors so obtained are compared with finite temperature experimental values.

Fundamental to these approaches is the assumption of the rigid pseudo-atom approximation viz. the electron density, including the valence electron density, can be partitioned to individual atoms and each such segment is frozen and moves rigidly with the thermal vibrations. This leads to the DW factor correction, the ‘fundamental step’ in the charge density studies. We note that Jones and March had raised concerns about the validity of the rigid pseudo-atom approximation for valence electrons.

In the rigid pseudo-atom approximation, since the valence charge densities move rigidly with thermal motion, it implies that there is no change in the valence electron wavefunctions and energies. It follows that the band gaps must be unchanged with temperature. This is contrary to experimental and theoretical observations. This is a simple demonstration of the incorrectness of the rigid pseudo-atom approximation for valence electrons in silicon and diamond. Hence, at present, there is no simple and theoretically justified method to obtain finite temperature valence charge densities.

In the Allen theory, the first step is to include the DW term in the pseudopotential form factor and then calculate the electronic structure. That is, the wavefunctions and charge densities of valence electrons so ob-

![Graph of DOS vs E-EF](image-url)
FIG. 9: The charge density along the (110) plane for (a) diamond and (b) silicon. The charge density of the static lattice (0 K) is shown in the left panel, at 300 K in the middle panel and at 600 K in the right panel for both the materials.

tained are temperature dependent and not frozen. Thus, the Allen theory provides a simple way to go beyond the rigid pseudo-atom approximation to theoretically obtain finite temperature valence charge densities.

Further, in the Allen theory, the SE corrections to the electron energies are calculated from the results of the above step. That is, there is no further correction of the wavefunctions. Hence, the first (DW) step of the Allen theory is sufficient to obtain finite temperature valence charge densities.

Figure 9 plots the (pseudo) valence charge densities of (a) diamond (C\textsubscript{8}) and (b) silicon (Si\textsubscript{8}) at 0 K, 300 K and 600 K. It shows that the charge distribution in the bonding region is enhanced with an increase in temperature. In general, the charge delocalization in silicon increases with increasing temperature. It is interesting to note that the differences in the charge density distribution at 300 K and 600 K compared to that at 0 K are more for silicon than diamond. This is due to the much higher mean square displacements of silicon compared to diamond (Table I). In silicon, the charge density distribution at finite temperatures shows more accumulation of charges in the bonding region with a reduction in the charge density in the vicinity of the core region. With better exchange correlation functionals, which reduce the underestimation of the band gaps, a more accurate charge density distribution would be obtained. In diamond, a similar effect is observed with a minor gain in the charge densities in the covalent bonding region.

As is well known\cite{ref1,ref2}, the pseudopotential method only gives pseudo-valence charge densities. They are incorrect near the nuclei. However, away from the nuclei and in the valence region, the pseudo-valence charge densities are similar to the true valence charge densities\cite{ref1,ref2}. The finite temperature charge density information in the valence region is valuable as this is the region where bonding effects are strongly manifested. The pseudo-valence charge densities plotted in Fig. 9 thus go beyond the rigid pseudo-atom approximation. Therefore, if the experimental data can also be analyzed appropriately to obtain finite temperature experimental charge densities, they can be compared with the theoretical results obtained from the Allen theory, a comparison that goes beyond the rigid pseudo-atom approximation.

V. CONCLUSIONS

In this paper, we report the implementation of the Allen theory with \textit{ab initio} pseudopotentials in density functional total energy calculations to obtain the finite temperature thermally-averaged electronic structure without any additional increase in the computational complexity and cost. Our results on diamond and silicon show that both the direct and indirect band gaps exhibit the “Varshni effect” with temperature only when the \textit{ab initio} pseudopotentials satisfy an additional criterion, that of temperature transferability. The temperature transferability criterion is satisfied only in a small subset of the parameter space of static lattice in
Troullier-Martins pseudopotentials for diamond and silicon. In these materials, the temperature transferability is strongly affected by the choice of the cut-off radius and inclusion/exclusion of unbound 3d state in the pseudopotential generation configuration. The finite temperature indirect band gaps in diamond and silicon are seen to be highly sensitive to the choice of cut-off radius.

Our results on finite temperature electronic structure show that the thermal vibrations affect the electron energies throughout the valence and conduction bands. We have calculated the zero-point and higher temperature band gap shifts in diamond and silicon for temperatures up to 1000 K. We compared our results on direct band gap shifts with those obtained using the Allen-Heine theory for the contribution from the Debye-Waller formalism to obtain finite temperature valence electron charge densities. The finite temperature charge densities obtained using Allen theory go beyond the rigid pseudopotential approximation, a limitation of the present methods used in charge density studies.

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