Symmetry-adapted tight-binding electronic structure analysis of carbon nanotubes with defects, kinks, twist, and stretch

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Abstract

In this paper, a symmetry-adapted method is applied to examine the influence of deformation and defects on the electronic structure and band structure in carbon nanotubes. First, the symmetry-adapted approach is used to develop the analog of Bloch waves. Building on this, the technique of perfectly matched layers is applied to develop a method to truncate the computational domain of electronic structure calculations without spurious size effects. This provides an efficient and accurate numerical approach to compute the electronic structure and electromechanics of defects in nanotubes. The computational method is applied to study the effect of twist, stretch, and bending, with and without various types of defects, on the band structure of nanotubes. Specifically, the effect of stretch and twist on band structure in defect-free conducting and semiconducting nanotubes is examined, and the interaction with vacancy defects is elucidated. Next, the effect of localized bending or kinking on the electronic structure is studied. Finally, the paper examines the
effect of 5–8–5 Stone–Wales defects. In all of these settings, the perfectly matched layer method enables the calculation of localized non-propagating defect modes with energies in the bandgap of the defect-free nanotube.

Keywords
Multiscale mechanics, objective structures, electronic structure, nanotubes, electromechanics

1. Introduction
The electronic properties of nanotubes have been a focus of research for over two decades, owing to the richness of the physics and potential applications [1–11]. An important feature of nanotubes is that their electronic properties have been found to be very sensitive to the chirality of the nanotube [12–16]. The aim of this paper is to develop a symmetry-adapted electronic structure method, based on tight-binding, to examine the behavior of nanotubes that are uniformly deformed. While this has been studied by other groups, notably including [17–22], we build further on the symmetry-adapted approach to develop a method to study defects, such as vacancies, Stone–Wales defects, and geometric defects, such as localized bending or kinking. Our approach to studying defects in a computationally tractable manner uses perfectly matched layers (PMLs) [23], which have been used to truncate the computational domain for wave equations posed on large or unbounded domains in other contexts, such as elastodynamics [24] and electromagnetism [25]. Specifically, PMLs provide a strategy to truncate the domain by using dissipative layers near the boundary of the truncated domain. By using an appropriate construction of the dissipative layers, there are no spurious reflections and standard Dirichlet boundary conditions can be applied on the outer boundary of the truncated domain. Other methods to account for defects in electronic structure calculations—in the setting of crystals—include flexible boundary conditions [26] and real-space methods [27]. Field-theoretic methods have been useful in providing insights in the setting of graphene and nanotubes [28–31].

Our symmetry-adapted approach builds on the objective structures (OS) framework introduced by James [32], and developed further by Dumitrică, James, and others [33–36]. The OS approach provides a simple and physical way to apply uniform deformations, such as twist and stretch. Further, using the OS framework, it can be demonstrated that the tight-binding Schrödinger equation satisfies an analog of the Bloch theorem in crystals, even when there is uniform twist or stretch. Prior work has shown that, even in the defect-free case, stretching is expected to lead to significant changes in the electronic properties [37]. Theoretical and experimental work has also shown that defects, such as Stone–Wales defects, can have unusual effects on the electronic structure [38, 39]. In this work, we study a combination of these settings. Specifically, we study the influence of stretch and twist on conducting and semiconducting chiral and armchair nanotubes in the defect-free and defected settings; we examine the effect of localized bending or kinking on the defect modes; and we examine the electronic structure of 5–8–5 Stone–Wales defects.

1.1. Organization
In Section 2, we describe the symmetry-adapted geometry of nanotubes with twist, stretch, or bending. In Section 3, we describe the tight-binding method and parameters, the analog of Bloch waves in nanotubes, and the consequent method of PMLs to study defects. In Section 4, we apply the method to study the electronic structure under torsion and stretch of defect-free nanotubes and nanotubes with a vacancy defect. In Section 5, we apply the method to a nanotube with localized bending or a kink. Finally, in Section 6, we examine a 5–8–5 Stone–Wales triplet.

2. Symmetry-adapted description of carbon nanotubes
A compact and practical symmetry-adapted description of carbon nanotubes is provided by the OS framework [32]. We build on this framework to develop a geometric description of deformed nanotubes.

Using the theory of isometry groups in 3D, following [34, 35, 40] (K Dayal, RS Elliott, and RD James, unpublished work, 2020), a discrete group $G$ of isometries consists of elements of the form $g = (Qc)$, where $Q$ is an orthogonal transformation and $c$ is a vector. The action of these isometries on any point $x$ is given by $g(x) = Qx + c$. 
We use the action of an isometry on a point to infer the successive action of group elements using composition of mappings:

\[ g_1(g_2(x)) = Q_1(Q_2 x + c_2) + c_1 = Q_1 Q_2 x + Q_1 c_2 + c_1 = g_1 g_2(x). \] (1)

This provides a natural definition for the group operation: given any two group elements \( g_1 = (Q_1 | c_1) \) and \( g_2 = (Q_2 | c_2) \), the group operation is \( g_1 g_2 = (Q_1 Q_2 | Q_1 c_2 + c_1) \). The group operation also enables us to define the identity \( Id = (I | 0) \) and inverses \( g^{-1} = (Q^* | -Q^* c) \).

We now apply the group-theoretic framework to a nanostructure that can be described by the OS framework. Consider a unit cell with \( M \) atoms, and label the positions \( x_{0,k}, k = 1, \ldots, M \), where the subscript 0 denotes the simulated unit cell. The non-simulated images are obtained using the formula

\[ x_{i,k} = g_i(x_{0,k}) = Q_i x_{0,k} + c_i, \quad g_i \in G, \quad k = 1, 2, \ldots, M. \] (2)

Given an isometry group \( G = \{g_0 := Id, g_1, \ldots, g_{N-1}\}, g_i = (Q_i | c_i) \), with \( N \) being the number of image unit cells that could be either infinite or finite, this formula gives us a description of the entire structure.

Specializing this to single-wall carbon nanotubes, following [34], we consider a nanotube with chirality described by \((n, m)\) and nanotube axis \(e\). Define the integers \(p\) and \(q\) such that \(pm_1 - qn_1 = 1\), where \(m_1 = m/GCD(n, m)\), \(n_1 = n/GCD(n, m)\) and \(GCD(n, m)\) is the greatest common divisor of \(n\) and \(m\). We can then define the generators \(h_1, h_2\) of this nanotube as isometries of the form

\[
\begin{align*}
  h_1 &= (R_{\theta_1} | (I - R_{\theta_1}) \ a), \quad R_{\theta_1} e = e, \quad 0 < \theta_1 = \frac{2\pi \min(|p|, |q|)}{GCD(n, m)} \leq 2\pi, \\
  h_2 &= (R_{\theta_2} | (I - R_{\theta_2}) \ a + \kappa_2 e), \quad R_{\theta_2} e = e, \quad \theta_2 = \pi \frac{p(2n + m) + q(n + 2m)}{n^2 + m^2 + nm}, \quad \kappa_2 = 3 \frac{GCD(n, m)}{2\sqrt{n^2 + m^2 + nm}} l_0.
\end{align*}
\] (3)

The generator \(h_1\) is a rotation operation with axis coinciding with \(e\), and \(h_2\) is a screw operation with the orthogonal part having the axis coinciding with \(e\). The quantity \(l_0 = 0.142\) nm is the bond length of the graphite sheet before rolling. The radius of the nanotube is given by \(r_0 = l_0(\sqrt{3(m^2 + n^2 + mn)})/2\pi\).

The vector \(a\) defines the spatial location of the axis of the nanotube. That is, the axis of the nanotube, oriented along \(e\), passes through the point \(a\). To see this, we notice the action of \(h_1\) and \(h_2\) on a point \(x\):

\[
\begin{align*}
  h_1(x) &= R_{\theta_1} x + (I - R_{\theta_1}) a, \\
  h_2(x) &= R_{\theta_2} x + (I - R_{\theta_2}) a + \kappa_2 e.
\end{align*}
\] (4)

If \(x\) lies on the axis of the nanotube, i.e. \(x\) has the form \(a + \alpha e\), where \(\alpha\) is any real number, we find that it is mapped to a point on the axis:

\[
\begin{align*}
  h_1(a + \alpha e) &= a + \alpha e, \\
  h_2(a + \alpha e) &= a + \alpha e + \kappa_2 e.
\end{align*}
\] (5)

Hence, the line \(a + \alpha e\) is mapped to itself, defining the axis.

The isometry group \(G\) has elements \(h_1^{i_1} h_2^{i_2}\), where \(i_1\) and \(i_2\) go over all integers. As shown in [34], \(G\) provides an isometry group to generate a nanotube that can be written

\[ x_{(i_1, i_2), k} = h_1^{i_1} h_2^{i_2}(x_{(0,0), k}), \quad i_1, i_2 \in \mathbb{Z}; \quad k = 1, 2. \] (6)

In this description, the unit cell contains two carbon atoms and hence \(k = 1, 2\). The parameters \(x_{(0,0), k}\) are listed in [33].

We note certain features of the OS isometry group approach. First, OS enables facile molecular dynamics calculations of nanotubes that are chiral, whereas periodic boundary conditions would require extremely long unit cells. Imposed twist can also break translational symmetry completely, and would require, in principle, infinitely long unit cells with periodic molecular dynamics, but can be easily and efficiently handled with OS. Further, OS enables a transparent approach to the application of external loads that cause twisting and extension: the choices for \(h_1, h_2\) in equation (3) correspond to an unloaded nanotube; changing \(\theta_2\) would correspond to imposed twist, while changing \(\kappa_2\) would correspond to imposed extension, as we describe in the next section.
2.1. Nanotubes with stretching, twisting, and bending

The OS framework provides a simple strategy to impose twisting (torsion) and stretch, e.g. [18, 35, 40].

Twist is imposed by changing the value of $\theta_2$ for the screw transformation $h_2$ to a value different from the equilibrium value shown in equation (3). That is, to impose a twist angle of $\tau$ per unit length, the value of $\theta_2$ is increased by $\tau \kappa_2$, where $\kappa_2$ is the axial translation associated with $h_2$ described in equation (3).

Stretch is similarly imposed by changing the value of $\kappa_2$ away from the equilibrium value listed in equation (3). That is, to impose a stretch $\lambda$, we replace $\kappa_2$ by $\lambda \kappa_2$ in equation (3).

Combined stretch and twist is imposed simply by a combination of both of these operations.

We next consider bending. Uniform bending can be readily imposed by using a different symmetry-adapted description and changing the parameters in equation (3) to go between a uniform nanotube with axis $e_1$ and a uniform nanotube with axis $e_2$, with a gradual variation between these uniform end-states.

Consider a bend localized between the atoms numbered $N_1$ and $N_2$ along the helix. The axis of the nanotube is assumed to change linearly between $e_1$ and $e_2$ between these atoms:

$$e(i) = \frac{N_1 - i}{N_2 - N_1} e_1 + \frac{i - N_1}{N_2 - N_1} e_2, \quad \forall i \in (N_1, N_2). \quad (7)$$

Similarly, we use $a(i) = i \kappa_2 e_1$ for $i \leq N_1$, and assume that it varies in the bend as $a(i) = a(i - 1) + \kappa_2 e(i)$.

The variation of $e$ implies a corresponding variation in $R_{\theta_1}(i)$ and $R_{\theta_2}(i)$. We keep $\theta_1$ and $\theta_2$ unchanged, and change the axis of the rotation $e(i)$ using equation (7).

The generators from equation (3) will vary now vary along the nanotube, as

$$h_1(i) = (R_{\theta_1}(i)) \left( I - R_{\theta_1}(i) \right) a(i), \quad R_{\theta_1}(i)e(i) = e(i),$$

$$h_2(i) = (R_{\theta_2}(i)) \left( I - R_{\theta_2}(i) \right) a(i) + \kappa_2 e(i), \quad R_{\theta_2}(i)e(i) = e(i), \quad (8)$$

where $i$ is the exponent of the helical transformation $h_2$. We notice that this no longer forms a group and the resulting structure is not an objective structure, but closely approximates one outside of the localized bending region.

With these variable generators, the atomic positions $x_{(i,1),k}$ can be written

$$x_{(i,1),k} = h_2(i_2 - 1) x_{(0,1),k}, \quad \forall i \in (N_1, N_2). \quad (9)$$

$$x_{(i,1),k} = h_1(i_2 - 1) x_{(0,1),k}. \quad (10)$$

The generators now provide an operation to position an atom given the position of the previous atom, but since it is not a group, the order of operation cannot be changed; however, this is not simply a non-Abelian group because it violates the closure property of a group. Examples of bent nanotube geometries that can be generated with this formula are shown in Figure 1.

3. Tight-binding analysis of nanotubes

In this section, we describe the key details of the tight-binding approach (Section 3.1), the application to uniformly twisted and stretched nanotubes using the analogies between OS and perfect crystals (Section 3.2), and the application to bent nanotubes using PMLs (Section 3.3).

3.1. Tight-binding formulation

We start from the one-electron Schrödinger wave equation:

$$-\frac{1}{2} \nabla^2 \phi(x) + V(x) \phi(x) = E \phi(x), \quad (11)$$
where $\phi(x)$ is the electron wave function and $V(x)$ is the electrostatic potential. The tight-binding model decomposes the wave function in terms of the atomic orbitals [41]:

$$\phi(x) = \sum_{i_1,i_2,k,\alpha} c_{i_1,i_2,k,\alpha} \phi_{\alpha}(x - x_{(i_1,i_2),k}),$$

(12)

where $\phi_{\alpha}$ is the orbital shape function for the atomic orbital $\alpha$, and the indices $i_1, i_2$, and $k$ index the atoms in the manner described in Section 2.

All carbon atoms are $sp^2$ hybridized in nanotubes, as one 2s orbital together with the $2p_x$ and $2p_y$ orbitals generate three $sp^2$ orbitals. Each $sp^2$ orbital forms $\sigma$ bonds with the $sp^2$ orbitals of the neighboring carbon atoms. The one remaining electron per carbon atom in the $p_z$ orbital moves out of the plane to form $\pi$ bonds with the neighboring $p_z$ orbitals. The energy states associated with the in-plane $\sigma$ bonds do not influence the electronic properties of nanotubes [5]. However, the $\pi$ orbital energy states cross the Fermi energy level and hence play a key role in nanotube electronics [5, 42]. The change in configuration of nanotube, owing to torsion, bending etc., changes the relative orientation of these $p_z$ orbitals forming $\pi$ bonds, which in turn alters its electronic properties [17, 18]. Hence, only the $p_z$ orbitals are used for the tight-binding model in this paper. We adopt Gaussian-type shape functions, provided in equation (2.3) in [43], to numerically represent these orbitals.

3.2. Twisting and stretching of nanotubes without defects: Bloch wave analogs

Objective structures have numerous analogies to crystals, as described broadly in, e.g., [32–35, 40, 44]. These analogies have been utilized to study mechanical [44] and electromechanical [17, 45] behavior of nanotubes under stretch and torsion and to examine stability [46] and defects [47] of nanostructures under torsion. The key application of this analogy here is that we are able to restrict our calculations to a small repeating unit cell. In crystals, this is possible owing to the classical Bloch theorem [48]. Here, we describe the analog of the Bloch theorem in the nanotube setting using the symmetry-adapted objective structure formulation.

Consider a perfect nanotube, that is, infinitely long and straight with no defects. The electrostatic potential $V_p(x)$ in this setting has the same symmetry as the nanotube:

$$V_p(g^i(x)) = V_p(x), \quad \forall i \in \mathbb{Z},$$

(13)
where \( g \) is any element of the isometry group, and \( i \) runs over the set of integers \( \mathbb{Z} \).

Using the one-electron Schrödinger model, we have

\[
-\frac{1}{2} \nabla^2 \phi(x) + V_p(x) \phi(x) = E \phi(x).
\]  

(14)

We show next, following the classical Bloch theorem, that the wave function \( \phi(x) \) does not inherit the symmetry of \( V_p \) from equation (13), but instead picks up a phase factor.

Following the general structure of the classical Bloch theorem [48], we begin by introducing two functionals \( \Pi_1 \) and \( \Pi_2 \), which operate on any function \( \chi(x) \) as \( \Pi_1 [\chi(x)] = \chi(h_1(x)) \) and \( \Pi_2 [\chi(x)] = \chi(h_2(x)) \). We notice that \( \Pi_1^i [\chi(x)] = \chi(h_1^i(x)) \) and \( \Pi_2^i [\chi(x)] = \chi(h_2^i(x)) \), where the superscript denotes the exponent defined as composition of mappings.

Considering the action of \( \Pi_1 \) on the Hamiltonian \( H \), we have

\[
\Pi_1 H \phi(x) = \Pi_1 \left[ \left( -\frac{1}{2} \frac{\partial^2}{\partial x_i \partial x_j} + V_p(x) \right) \phi(x) \right] = \left( -\frac{1}{2} \frac{\partial^2}{\partial (h_1(x))_i \partial (h_1(x))_j} + V_p(h_1(x)) \right) \phi(h_1(x)),
\]  

(15)

where subscripts denote components and repeated indices imply summation. From equation (13), we have \( V_p(h_1(x)) = V_p(x) \). From [32, 33], we have that

\[
\frac{\partial}{\partial (h_1(x))_i} = (R_{h_1})_{ij} \frac{\partial}{\partial x_j} \Rightarrow \frac{\partial^2}{\partial (h_1(x))_i \partial (h_1(x))_j} = (R_{h_1})_{ij} (R_{h_1})_{kl} \frac{\partial^2}{\partial x_j \partial x_l} = \frac{\partial^2}{\partial x_i \partial x_j},
\]  

(16)

where \( R_{h_1} \) is the orthogonal transformation corresponding to \( h_1 \), introduced in equation (3). Therefore, we have

\[
\Pi_1 H \phi(x) = \left[ \left( -\frac{1}{2} \frac{\partial^2}{\partial x_i \partial x_j} + V_p(x) \right) \Pi_1 [\phi(x)] \right] = H \Pi_1 [\phi(x)].
\]  

(17)

That is, \( H \) and \( \Pi_1 \) commute. Through an exactly analogous calculations, we can show that \( H \) and \( \Pi_2 \) commute.

A consequence of the commutation relation is that \( H, \Pi_1, \Pi_2 \) have a common set of eigenfunctions [48]. Hence, \( \phi(x) \), an eigenfunction of \( H \), is also an eigenfunction of \( \Pi_1 \) and \( \Pi_2 \):

\[
\Pi_1 [\phi(x)] = t_1 \phi(x) \Rightarrow \Pi_1^{i_1} [\phi(x)] = t_1^{i_1} \phi(x), \quad \forall i_1 \in \mathbb{Z},
\]  

(18)

\[
\Pi_2 [\phi(x)] = t_2 \phi(x) \Rightarrow \Pi_2^{i_2} [\phi(x)] = t_2^{i_2} \phi(x), \quad \forall i_2 \in \mathbb{Z}.
\]  

(19)

where \( t_1 \) and \( t_2 \) are the eigenvalues of \( \Pi_1 \) and \( \Pi_2 \) corresponding to the eigenfunction \( \phi \). It follows immediately that

\[
\Pi_1^{i_1} \Pi_2^{i_2} [\phi(x)] = \Pi_2^{i_2} \Pi_1^{i_1} [\phi(x)] = t_2^{i_2} t_1^{i_1} \phi(x).
\]  

(20)

We first consider \( t_1 \). Notice that \( h_1^{N_1} = (I|0) \), where \( N_1 = 2\pi/\theta_1 \), i.e., if we apply the rotation operation \( N_1 \) times, we recover the identity operation. Therefore,

\[
\Pi_1^{N_1} [\phi(x)] = t_1^{N_1} \phi(x) = \phi(x) \Rightarrow t_1^{N_1} = 1 \Rightarrow t_1 = e^{i \frac{2\pi n}{N_1}}, \quad n \in \{0, 1, \ldots, N_1 - 1\}.
\]  

(21)

Using \( N_1 = 2\pi/\theta_1 \) and defining \( k_1 = n/r_0 \), we can write

\[
t_1 = e^{ik_1 \theta_1 r_0}, \quad k_1 r_0 \in \{0, 1, \ldots, N_1 - 1\}.
\]  

(22)

The arbitrary quantity \( k_1 \) has the natural interpretation of an angular wavenumber.

We next consider \( t_2 \). Unlike \( h_1 \), no power of the screw operation \( h_2 \) gives the identity operation, and all integer powers must be considered. We first define \( \gamma_2 \) as the length between two consecutive atoms along the helix:

\[
\gamma_2 = \sqrt{r_0^2 \theta_2^2 + \kappa_2^2}.
\]  

(23)

Consider the eigenvalues \( T_2(i_2 \gamma_2), T_2(j_2 \gamma_2), T_2((i_2 + j_2) \gamma_2) \) corresponding to the operations \( \Pi_2^{i_2}, \Pi_2^{j_2}, \Pi_2^{i_2+j_2} \), respectively; notice that these operations correspond to moving along the helix by a distance \( i_2 \gamma_2, j_2 \gamma_2, (i_2 + j_2) \gamma_2 \),
respectively. Since it is equivalent whether we move in two successive steps of \( t_1 \gamma_2, j_2 \gamma_2 \) or directly by \((t_1 + j_2)\gamma_2\), we have that \( T_2(t_1\gamma_2) \times T_2(j_2\gamma_2) = T_2((t_1 + j_2)\gamma_2)\). Therefore, \( T_2 \) must be an exponential in its arguments; further, since \( T_2(t_2\gamma_2) \) must be bounded for all \( t_2 \in \mathbb{Z}\), it must have unit magnitude. Therefore, \( T_2(t_2\gamma_2) = e^{i k_2 \gamma_2} \), giving:

\[
t_2 = e^{i k_2 \gamma_2}, \quad k_2 \gamma_2 \in [-\pi, \pi).
\]

The arbitrary quantity \( k_2 \) has the natural interpretation of a helical wave number.

By substituting equations (22) and (24) in equation (20), we obtain the Bloch theorem analog for nanotubes:

\[
\Pi_{1,2}^{(i)} \rho_{1,2}^{(i)} [\phi(x)] = \phi \left( h_{1,2}^{(i)}(x) \right) = e^{i k_1 \gamma_1 t_1 + i k_2 \gamma_2} \phi(x).
\]

Using the linear combination of atomic orbitals (LCAO) approach, we can rewrite the form of equation (25) as

\[
\phi_{\alpha,1,2}(x) = \sum_{\alpha,m,j_1,j_2} c_{\alpha m} e^{i j_1 \gamma_1 t_1 + i j_2 \gamma_2} \phi_\alpha(x - x_{j_1,j_2,m}),
\]

where \( \alpha \) denotes the atomic orbital. This can be substituted in equation (14) for the numerical calculation of Bloch wave analog solutions. The Bloch theorem analog developed here is applicable to infinite nanotubes subject to uniform stretch or torsion, and also provides the analog of band structures and density of states (DOS), which we apply to carbon nanotubes in Section 4.1.

### 3.3. Nanotubes with defects: Perfectly matched layers

The Bloch wave analogs developed in Section 3.2 are restricted to infinite nanotubes that are uniformly deformed but without defects. To enable the study of defects, we build on the Bloch wave analogs and use the PML approach, following [23], using the complex coordinate stretching approach [49]. This approach enables us to focus the computational effort in the neighborhood of the defect and truncate at some distance away, with the perfect matching preventing the formation of spurious reflections and size effects, owing to the finite domain.

We recall the single-electron Schrödinger wave equation given by

\[
-\frac{1}{2} \nabla^2 \phi(x) + V(x) \phi(x) = E \phi(x). \tag{27}
\]

For perfect OS with no defects, the Bloch wave analog can be written as

\[
-\frac{1}{2} \nabla^2 \phi_k(x) + V_p(x) \phi_k(x) = E_k \phi_k(x), \tag{28}
\]

where \( k = (k_1, k_2) \) is the Bloch wave vector.

In the presence of a localized (i.e., non-extended) defect, the electrostatic potential \( V(x) \) is decomposed into \( V_p(x) + V_d(x) \), where \( V_p \) is the potential of the perfect structure and \( V_d \) is the defect potential. Similarly, we decompose the wave function into \( \phi(x) = \phi_k(x) + \psi(x) \), where the first term corresponds to the incoming Bloch wave and is obtained from equation (28), and \( \psi \) is the scattered wave. Using this decomposition in equation (27), we get

\[
-\frac{1}{2} \nabla^2 (\phi_k(x) + \psi(x)) + (V_d(x) + V_p(x)) (\phi_k(x) + \psi(x)) = E (\phi_k(x) + \psi(x)). \tag{29}
\]

Noticing that the scattered wave \( \psi(x) \) must vanish at \( |x| \to \infty \), equation (29) reduces, at \( |x| \to \infty \), to

\[
-\frac{1}{2} \nabla^2 \phi_k(x) + V_p(x) \phi_k(x) = E_k \phi_k(x), \quad \text{at } |x| \to \infty. \tag{30}
\]

Comparing equation (30) with equation (28), we deduce that \( E = E_k \); this is to be expected, as the scattering is elastic and, therefore, no energy is lost. Using that \( E = E_k \), we can subtract equation (28) from equation (29) to obtain

\[
-\frac{1}{2} \nabla^2 \psi(x) + [V_d(x) + V_p(x)] \psi(x) + V_d(x) \phi_k(x) = E_k \psi(x). \tag{31}
\]
We notice that this is not an eigenvalue problem. Rather, we first solve equation (28) as an eigenvalue problem to find the energy $E_k$ and wavefunction $\phi_k$ of the incident wave, given $k$, using the Bloch wave approach developed in Section 3.2, and then use that information in equation (31) to solve a standard linear problem for $\psi$.

To solve equation (31) numerically, we develop the weak form

$$
\int_{\Omega} \left[ \frac{1}{2} \nabla \psi^* \cdot \nabla \psi + \psi^*(x) \left( V_p(x) + V_\sigma(x) - E_k \right) \psi(x) \right] dV - \int_{\Gamma} \frac{1}{2} \psi^*(x) \nabla \psi(x) \cdot \hat{n} ds = - \int_{\Omega_d} \psi^*(x) V_d(x) \phi_k(x) dV.
$$

(32)

In this equation, $\psi^*$ is the complex conjugate of $\psi$; $\Omega_d$ is the bounded region where $V_d$ is nonzero; $\Omega$ is the computational domain that includes the defect as well as the surrounding region; and $\Gamma$ is the boundary, with outward unit normal $\hat{n}$, of $\Omega$. If $\Omega$ is taken to be sufficiently large, we can apply Dirichlet boundary conditions on $\Gamma$ as the scattered wave would decay, but this would require a very large computational expense. Instead, we solve equation (31) in a relatively small domain near the defect, and construct a thin perfectly matched layer in the vicinity of the boundary. Perfectly matched layers cause the scattered wave to decay quickly without spurious reflections into the interior of the domain, and we can safely apply Dirichlet boundary conditions on $\Gamma$.

We use a fictitious coordinate transformation such that each point $x$ in real space is mapped to $\tilde{x}$:

$$
\tilde{x} = x + i \sigma(x).
$$

(33)

The real smooth function $\sigma(x)$ is chosen to be 0 outside the PML, and chosen to have the form [23]

$$
\sigma(x) = \sigma_0 \int_{x_0}^{x_1} |(t - x_0)|^2 |(x_1 - t)|^2 dt
$$

(34)

within the PML. Here, $x_0$ is a point at the interface of the computational domain and the absorbing layer, and $x_1$ is a point on the exterior boundary. To accommodate this transformation, the weak form in equation (32) is written as

$$
\int_{\Omega} \left[ \frac{1}{2} \psi^* F_{ij}^{-1} \psi \chi \left( V_p(x) + V_\sigma(x) - E_k \right) \psi(x) \right] J dV = - \int_{\Omega_d} \psi^*(x) V_d(x) \phi_k(x) J dV,
$$

(35)

where repeated indices denote summation, $F_{ij} = \partial \tilde{x}_i / \partial x_j$, and $J = \det F$. The integral over $\Gamma$ vanishes, owing to the applied Dirichlet boundary conditions.

The PML approach described here is useful to compute the scattering resulting from incident electrons. However, defect modes, i.e. eigenstates of the Schrödinger equation that are in the bandgap of the perfect structure and hence localized to the defect, are also of interest. To compute defect modes, we directly solve equation (27) as an eigenvalue problem, within a truncated domain using PMLs, without decomposing the potential or wavefunction.

4. Stretched and twisted nanotubes with defects

We now apply the framework developed in the previous section to study the effect of twisting and stretching on nanotubes of different chiralities, both defect-free as well with a vacancy defect. Bloch wave analogs are used to obtain band structures for homogeneously deformed nanotubes of various chiralities, while PMLs are utilized for analyzing the influence of vacancy. Introducing stretch, torsion, or changes in chirality induces significant changes in band structure and electron density.

4.1. Density of states for nanotubes of various chiralities under torsion and stretch

The band structures reported here are obtained by solving the Bloch wave analogs. The DOS, $D(E)$, is calculated following [50]

$$
D(E) = \frac{1}{\sqrt{2\pi} \sigma} \sum_i e^{-(E-E_i)^2/2\sigma^2},
$$

(36)
corresponding to the energy state $E$, where the expression is summed over $i$ for each energy level $E_i$; $\sigma$ is a smoothing parameter, which is taken to be $2 \times 10^{-3}$.

Both conducting and semiconducting nanotubes are probed under twist and stretch. A chiral (4, 2) nanotube is used as a representative of chiral semiconducting nanotubes, while a (5, 5) armchair nanotube is used as a representative of conducting nanotubes. Figure 2 shows the band structure for a (4, 2) chiral nanotube, selected for its semiconducting properties. The energy is plotted against $k_2$, for several representative values of $k_1$. Since $N_1 = 2$ for a (4, 2) carbon nanotube, the band structure is plotted for two independent values of $k_1$, following equation (22). As expected in (4, 2) nanotubes, we observe a bandgap.

We then subject the nanotube to torsion and stretch. Figure 3 shows the DOS under different levels of torsion and stretch. We observe a significant variation of electronic properties in Figure 3(top) under torsion for a (4, 2) chiral nanotube. We see that the bandgap changes slightly for a twisting of $1^\circ$/nm, but disappears completely at a twisting angle $4^\circ$/nm; the corresponding band structure under a twist of $4^\circ$/nm is shown in Figure 4. However, significant qualitative changes owing to stretching are not observed in Figure 3(bottom); roughly speaking, the DOS simply translates in energy space.

Thus, we observe that the bandgap of a semiconducting nanotube can disappear under sufficient levels of twist. We next turn to the case of a (5, 5) conducting armchair nanotube, and find that a bandgap can appear under sufficient levels of twist.

Figure 5 shows the band structures of a (5, 5) nanotube with no twist and with a twist of $2^\circ$/nm, respectively, with $N_1 = 5$ cases of $k_1$ for each case. We observe that a bandgap is introduced in response to a $\pm 2^\circ$/nm twist in the conducting (5, 5) armchair nanotube. We point out that positive and negative twist provide atomic structures that are related by mirror symmetry, and hence have the same band structure.

The effect of twisting on band structure observed here agrees with the theoretical results given by [37] and computational findings [17] on the twisting of armchair nanotubes. In general, we find that qualitative changes in the band structure can be induced by torsion. These changes can be physically understood by noticing that twisting has a qualitatively similar effect to a change in chirality. Relative rotation of $\pi$ orbitals induced in neighboring atoms as a result of twisting causes this change in electronic properties. Conversely, we see that stretching causes fewer qualitative changes to the band structure. Similar ideas have been investigated in strain engineering of the graphene band structure using density functional theory [51], Green’s function techniques [52], and experimentation [53].

4.2. Influence of vacancy defects

We next study the influence of stretch, torsion, and chirality on the electron structure of nanotubes with vacancy defects. When defects are present, the symmetry is broken; hence, we use the PML method described in Section 3.3. We use this to obtain the electron density, and study the influence of torsion, stretch, and chirality on the electron density.

Figure 6 shows the scattered electron density for a twisted (5, 5) armchair nanotube with a vacancy defect subject to a twist of $3^\circ$/nm. To show the effect of stretch and torsion, Figure 7 shows the maximum electron
Figure 3. Density of states (DOS) for (4,2) chiral nanotube under varied amount of (top) torsion and (bottom) stretch, with bandgap highlighted for torsion.

Figure 4. Band structure of (4,2) nanotube under $4^\circ$/nm twist for different values of $k_1$. The Fermi energy level is shown with a dotted line.

density in the (5, 5) armchair nanotube with a vacancy for different levels of twist and stretch. In Figure 7(left), the level of stretch is varied with a constant pre-twist of $3^\circ$/nm, while Figure 7(right) shows the effect of the twist angle. The continuous lines in Figure 7 are obtained by a curve fit. Figure 7(left) shows that both axial
Figure 5. Band structures for a (5,5) armchair nanotube: (a) no twist; (b) twist of $\pm 2^\circ/\text{nm}$. The Fermi energy levels are shown with dotted lines.

Figure 6. Scattered electron density in a (5,5) nanotube with vacancy defect with a twist of $3^\circ/\text{nm}$. All lengths are in angstroms.

Figure 7. Influence of stretch and torsion on the maximum electron density: left, stretch is varied, with a constant pre-twist of $2^\circ/\text{nm}$; right, twisting angle is varied. The lines are fits to the data points.

tension and compression have a tendency to increase the maximum electron density in comparison with the undeformed configuration. Torsion has a more complex effect on maximum electron density, as observed in Figure 7(right). We observe that, while twisting, the maximum electron density gradually decreases initially with the increase of twist angle, followed by a sharp increase and then a decrease again. The twist angle was limited to $5^\circ/\text{nm}$ to avoid torsional buckling at higher twist angles [44].
Figure 8. Reflectional symmetry observed in the scattered electron density patterns of two mutually reflectionally symmetric nanotubes, for (2,5) on the left and (5,2) on the right, for the same incident Bloch wave of \( k_1 = 0 \) and \( k_2 = .347435 \). All lengths are in angstroms.

We next study the role of chirality of the nanotube. Figure 8 shows the electron density for (2, 5) and (5, 2) chiral nanotubes. These nanotubes are chosen since they are examples of exact reflected copies of each other. The electron density plots are mirror images of each other, as these nanotubes are related by a reflection.

In Figures 6 and 8, we also observe a repeating pattern in the electron density, except for the sharp jump near the defect. This is caused by the dependence of the scattering wave function \( \psi(x) \) on the Bloch wave function \( \phi_k(x) \), as shown in equation (31). The Bloch waves inherit the symmetry of the nanotube, which is passed on to the scattered wave function.

5. Defect modes in kinked nanotubes

We next examine kinked nanotubes, with the geometric description from Section 2.1. Unlike uniformly bent nanotubes, e.g. [33], kinked nanotubes must be considered as containing a geometric defect. To obtain the defect modes, we use the PML method to focus on a region in the vicinity of the kink. We focus on the chiral (4, 2) semiconducting nanotube and armchair (5, 5) conducting nanotube, as in the previous section, to enable comparisons. Prior work [54, 55] in semiconducting nanotubes has shown the possibility of additional defect modes in the bandgap, owing to bending.

Figure 1 shows the dependence on angle of kinking of a specific mode in a (5, 5) nanotube. We observe that the localization of the eigenstates increases with the sharpness of kinking.

We next turn to the (4, 2) chiral nanotube, which has a bandgap. Figure 9 shows a defect mode that corresponds to the energy eigenvalue within the bandgap. These additional modes within the bandgap are solely due to the defect [54–57]. The PML-based approach enables us to compute the corresponding electronic structure.

6. Defect modes induced by a Stone–Wales defect

Stone–Wales defects are of significant interest, owing to their frequent occurrence in carbon nanotubes. The most common Stone–Wales defect found in graphene is 5–7–7–5, where four adjacent hexagons reconstruct themselves into two pentagons and two heptagons. However, the 5–8–5 Stone–Wales defects—corresponding to a relaxed bivacancy—have received recent attention and are relatively less understood [38, 39, 58]; therefore, we use the PML method to study the defect modes in a cluster of these defects. Three 5–8–5 Stone–Wales defects are constructed such that they meet at a common point, as shown in Figure 10, motivated by the molecular dynamics simulations of similar configurations in graphene [39].

We consider a chiral (6, 8) nanotube. To construct the 5–8–5 defect cluster, we remove a pair of carbon atoms, and relax the structure using molecular dynamics simulations using LAMMPS with the microcanonical ensemble. We then use the PML method on this relaxed configuration to find the defect modes; some examples are shown in Figure 11. All of these modes lie in the bandgap of the (6, 8) nanotube and do not correspond to
any Bloch wave solution. These results qualitatively match the electronic structure of a nanotube with 5–7–7–5 Stone–Wales defects in [59].

7. Conclusion
In this paper, we used the symmetry-adapted OS framework to obtain the analog in nanotubes of classical Bloch waves, and built on this to develop a perfectly matched layer method for defects in the setting of tight-binding. The nanotube geometries that result from the deformation or the intrinsic chirality can be non-periodic, or only
periodic with the use of large unit cells. However, the symmetry adaptation uses isometric transformations—namely, screw and rotation operations—to describe all kinds of nanotubes, as well as transparently account for deformations.

We applied the symmetry-adapted Bloch wave analogs to compute band structures for stretched and twisted nanotubes with different chiralities. The resulting band structures and densities of states show the significant effect of twist on electronic properties of nanotubes; torsion can observably reduce the bandgap, or even cause it to vanish in a semiconducting chiral nanotube, as well as introduce a bandgap in a conducting armchair nanotube; twisting and changes in chirality have qualitatively the same effect. These findings agree with the analytical results provided by [37].

We then studied the effects of selected defects on the electronic structure and electromechanics. The lack of symmetry induced by the presence of the defect requires large computational domains to avoid spurious size effects. We therefore apply PML to obtain a computationally tractable approach, allowing us to truncate the domain without spurious boundary effects. We apply this to study the scattering of Bloch waves at vacancies in nanotubes, and also to study the interaction with twist and stretch for different chiralities.

We next examined localized bending or kinking, treated as a geometric defect, in both armchair and semiconducting chiral nanotubes. The findings agree well with the experimental observations of [60]. We also compare our results with computational results reported in the literature [17, 56, 57, 59]. These works have largely focused on semiconducting nanotubes, with the observation that defect modes appear in the bandgaps, owing to bending. The PML method enables us to examine the spatial structure of the defect modes in greater detail.

Finally, we examined a combination of three 5–8–5 Stone–Wales defects in a semiconducting chiral nanotube. Various prior works have examined the DOS plot to find defect modes [54–57], and the PML method enabled us to probe the spatial structure of the defect modes.

In future work, the use of symmetry-adapted PML methods can be applied to the setting of the linear scaling multiple scattering (LSMS) formulation of density functional theory [61]. The LSMS approach relies heavily on the wave scattering picture of quantum mechanics, thereby providing a natural framework for the use of PML-based methods.

Research data
A version of the code developed for this work is available at github.com/soumyam-code/Tight-binding-nanotube.

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