Ewald summation on a helix: A route to self-consistent charge density-functional based tight-binding objective molecular dynamics

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-Popular Summary-

When Paul Peter Ewald penned his summation method in 1921, it is unlikely that he would have foreseen the use of computers to simulate crystals at the atomistic level, let alone the impact of his method on this field. Ewald summation is essential to many atomistic simulation techniques and has enabled countless discoveries of material properties. However, like many other atomistic tools, the classical Ewald summation is dependent on the translational symmetry of crystalline solids. Often, the most fundamental symmetry in biomolecules and nanostructures is not translational, but helical. Can the Ewald ‘s method be adapted to the helical case? In this paper, we demonstrate that such a generalization is feasible and can enable efficient nanostructure and biomolecule simulations. Because nanostructures and biomolecules exist on a scale comparable to interatomic distances, atomistic detail is essential to understanding their behavior. Thus, improving the capability of atomistic simulations to describe these structures represents a significant breakthrough.

Currently, helical structures are simulated using a large number of atoms, either by artificially imposing translational periodicity, or by considering an isolated cluster. In contrast, we employ a small number of atoms replicated with an arbitrary combination of rotation and translation operations, representing an infinite helical structure that may not possess any pure translational periodicity. Combined with the generalized Ewald summation, this allows us to use self-consistent quantum-mechanical interaction models.

The exact methodology presented can be used to study a wide variety of bio- and nanostructures in a new manner, while the generalized Ewald summation can enable other types of helical calculations, ranging from empirical to first-principles.
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(Dated: May 4, 2013)

Abstract

We explore the generalization to helical case of the classical Ewald method [1], the harbinger of all modern self-consistent treatments of waves in crystals, including \textit{ab initio} electronic structure methods. Ewald-like formulas for the electrostatic potential and van der Waals energy prove to be numerically tractable and able to provide the crucial component needed for coupling objective molecular dynamics [2] with the self-consistent charge density-functional based tight-binding [3] treatment of the interatomic interactions. The robustness of the method in addressing complex heteronuclear nano and bio-systems is demonstrated with illustrative simulations on a helical boron nitride nanotube, a screw dislocated zinc oxide nanowire, and an ideal DNA molecule.
I. INTRODUCTION

A generalization of periodic molecular dynamics (MD) termed objective MD [2] provides a rigorous way of doing dynamic calculations on a restricted set of atoms placed under objective boundary conditions, which include helical (rotation and translation) boundary conditions. The method is applicable to a wide variety of molecular structures from the nano and bio areas united under the concept of objective structures [4]. Examples of such structures are carbon nanotubes and other nanostructures now being synthesized, including screw-dislocated nanowires [5], the tails and capsids of many viruses [6], ideal DNA, and amyloid fibrils [7]. To carry out objective MD simulations with forces derived from electronic structure on objective structures containing electrostatic atomic charges and microscopic dispersion forces, it is necessary to evaluate the electrostatic potential $V$ at a reference point located at $X = \{r'\cos\theta', -r'\sin\theta', T'\}$

$$V(X) = \sum_{\zeta=-\infty}^{+\infty} \frac{1}{|X - X_{\zeta}|},$$

and/or the dispersion part of the van der Waals energy

$$W(X) = \sum_{\zeta=-\infty}^{+\infty} \frac{1}{|X - X_{\zeta}|^6},$$

when $X_{\zeta}$ are equidistantly distributed over an ideal helix, Fig. 1(a), described by

$$X_{\zeta} = R^z X_0 + \zeta T, \quad \zeta = -\infty, ..., +\infty.$$  

In the above equation, there is a charge located at position $X_0 = \{r\cos\theta_0, -r\sin\theta_0, T_0\}$ in the $\zeta = 0$ cell. There is a singularity if $X$ coincides with positions $X_0$. The symbol $\sum'$ indicates that in this situation, the singular term $\zeta = 0$ is excluded from the summation.

The basic helical operation is defined by a rotation around the z-axis of angle $\theta$, described by matrix $R$,

$$R = \begin{pmatrix}
\cos\theta & -\sin\theta & 0 \\
\sin\theta & \cos\theta & 0 \\
0 & 0 & 1
\end{pmatrix},$$

and the axial vector $T = \{0, 0, T\}$ of magnitude $T$ oriented along the z-axis.

The direct numerical summations (1) and (2) are computationally inefficient and become intractable in the context of molecular dynamics and electronic structure calculations. In
bulk, Ewald [1] techniques [8–10] are currently utilized to evaluate such summations. These are mixed space approaches based on the classical Ewald method presented in diverse textbooks [15, 16]. The short range contributions is evaluated in real space and the long range part is converted into a reciprocal space sum that is also fast converging. Originally proposed in three dimensions, the method has been generalized to one and two dimensions [11–14]. The utility of a helical Ewald approach has not been yet explored.

The fundamental problem of evaluating the electrostatic field generated by discrete charges distributed over an ideal helix is encountered in a number of areas of modern science. For example in condensed matter physics, it is highly relevant for chiral charge-density waves [17] and for understanding the spin selective transport in helical molecular systems [18]. In biological physics and soft matter, this problem is important in understanding the relation between the helical structural and the generated local electric field [19–21], the electrostatic interaction between biological helices [22], and the electrostatic-driven helical patterns formed in fibers, nanotubes, and pores [23]. With the Green-function technique and cylindrical and helical coordinates, analytical solutions have been derived. Unfortunately, these formulas are quite complex and appear less usable in practice, especially when they are expressed in terms of helical Bessel functions [24]. Similar to the approach explored here, the pair interaction for parallel discrete biological helices has been examined based on truncated Fourier expansions of the discrete Coulomb sums [25].

Our particular objective is to enable microscopic calculations in objective structures within the self-consistent charge (SCC) density-functional based tight-binding (DFTB) scheme [3]. Note that the coupling of objective MD with the earlier method, the two-center non-orthogonal TB and DFTB potentials [26] extended to capture dispersion forces within the cutoff approximation, was already achieved [27, 28]. This non-SCC-DFTB objective MD methodology was successfully utilized so far in homonuclear structures such as hexagonal, polycrystalline and screw-dislocated silicon nanowires [28, 29], carbon nanotubes [30–32], graphene [34] and graphene nanoribbons [35], and often allowed for new insights. Unfortunately, the non-SCC-DFTB level of chemistry is insufficient to tackle the rich variety of available helical nano- and bio-structures (for a recent review see Ref. [36]) showing complex microscopic interactions, for describing large mechanical deformations, or for making credible predictions of new helical materials. The SCC-DFTB generalization is instead needed as it is more closely connected with first principles methods. As presented on several occa-
sions [3, 37, 38], SCC-DFTB offers a superior description of the chemical binding, especially in heteronuclear systems, while still being computationally efficient enough to allow for performing dynamical simulations. Both aspects are important for objective MD simulations. The SCC-DFTB description is superior to force field approaches and, in fact, it has been even used [37] as the high-level method in QM/MM simulations.

This paper is organized as follows. In Section II we present the Ewald formulas for Coulomb and dispersion sums, and discuss their applicability with one numerical example. In Section III we briefly indicate how these formulas are used in the SCC-DFTB machinery. The power of the resultant method is next illustrated with unprecedented simulations of a BN nanotube, a ZnO nanowire containing a screw dislocation, and an ideal DNA molecule. Section IV gives the conclusions.

II. THE HELICAL EWALD METHOD

A. Coulomb Sum

The approach investigated here is a direct generalization of the classical Ewald method [1]. To calculate sum (1), we use the identity

$$\frac{1}{|\mathbf{X} - \mathbf{X}_\zeta|} = \frac{1}{\sqrt{\pi}} \int_0^\infty t^{-1/2} \exp(-|\mathbf{X} - \mathbf{X}_\zeta|^2 t) dt,$$

(5)
FIG. 3: SCC-DFTB simulation of intrinsic twist of (4,2) BN nanotube. (a) Atomic structure and (b) objective computational domain. (c) Minimization of strain energy with respect to twist angle.

We find that our generalization to helical case of the classical Ewald approach is pivotal for SCC-DFTB calculations under the boundary conditions (19). The structural relaxations described next were carried out with the code DFTB+ [43]. The simulations were considered converged when the maximum force modulus was less than $10^{-4}$ Hartree/Bohr. We highlight that all of the presented simulations are inaccessible to current methods.

A. Chiral BN Nanotube

We first demonstrate the method for one-atom-thick heteronuclear nanotubes. In this system we demonstrate the suitability of the proposed electrostatic approach when $r \approx r'$ and angle $\theta$ is relatively large. It is known that the computational cost of chiral one-dimensional periodic systems, especially when performed at a quantum mechanical level, is rather high as nanotubes can contain a large number of atoms in the unit cell. The structure of nanotubes can be considered to be a rolled-up section of the planar sheet of the source material - for example, graphene in the case of carbon nanotubes and a hexagonal...
boron-nitride mono-layer in the case of BN nanotubes. It has recently been obtained with non-SCC-DFTB objective MD that a general (n,m) nanotube can lose the translational periodicity predicted by this rolled-up construction due to a shear strain manifested as an intrinsic structural twist; for such cases, simulations relying on translational symmetry would become even more demanding [33].

The rich objective symmetry which characterizes this class of materials, however, can drastically reduce their computational costs, if adequately exploited. Following the screw-dislocation procedure described before [30, 33] we calculate the optimal morphology of a (4,2) BN nanotube, Fig. 3(a), using a computational cell consisting of six B-N dimers (12 atoms) positioned along the roll-up vector, Fig. 3(b). The SCC treatment allows for better description of the partially ionic bonding in BN. We also used the most up to date DFTB parameters [46].

In order to achieve a tolerance of $< 10^{-10}$ Hartree with this configuration, we use the numerical parameters and maximum summation indices listed in Table I. To provide a margin of error, we increase the integration nodes and maximum summation indices - the bare minimum values required are listed in parentheses. Starting with the ideal roll-up configuration (modified to match each twist rate value we examine), we perform conjugate-gradient relaxations. These calculations involved two stages: We relaxed the atomic positions under twist angle $\theta$ at constant $T$. Next, we relax the twisted NT under parameter $T$ at the considered $\theta$. These simulations take only several minutes each on a single core.

The net charges on B and N atoms are $\pm 0.366$ e. The energy due to the Coulomb part of the SCC correction is -0.438 Hartree for the 12-atom unit cell. To test the validity of the Ewald method, we also evaluated this value using direct summation, and found perfect agreement. Direct summation over 4000 images in each direction is required to reach a tolerance of $< 10^{-10}$ Hartree, a significantly increased computational effort compared to the Ewald method. The total energy difference due to the introduction of SCC corrections, including the Coulomb interaction, the short-range corrections, and the self-consistent adjustment of the wavefunction expansions, is $+0.0231$ Hartree.

The ideal roll-up construction predicts values for $\theta$ and $T$ of $12.86^\circ$/cell and 2.466 Å/cell, respectively. As it can be seen in Fig. 3(c), the untwisted (rolled-up) morphology does not correspond to a metastable state, in agreement with previous predictions [33]. The analogous non-SCC simulations predicts a twist angle of $13.51^\circ$/cell and a length of 2.520 Å/cell. Our
FIG. 4: SCC-DFTB simulation of Eshelby twist of (3,0) ZnO nanowire. (a) Atomic structure and (b) objective computational domain. (c) Minimization of strain energy with respect to twist angle, showing Eshelby twist of 6.61°.

The present simulation predicts a very similar twist angle of 13.52°/cell, and a significantly differing (0.3% strain) length of 2.513 Å/cell.

B. Screw-Dislocated ZnO Nanowire

We now demonstrate the method in heteronuclear nanowires, when $\theta$ is small and $r \neq r'$ is possible. When a thin rod contains an axial screw dislocation, it becomes intrinsically twisted [47]. Interestingly, all the experimentally observed nanowires containing axial screw dislocations were also twisted [5]. With standard methods, one can efficiently simulate only ideal nanowires by considering their translational periodicity $T$ and accounting for the small number of atoms $M$ located in one primitive cell. The generated twist (unknown beforehand) prevents the applicability of the standard periodic boundary conditions treatment. Thus, objective MD is necessary to model screw-dislocated nanowires in their fully relaxed configuration. In refs. [48, 49], we approached this problem with the non-SCC treatment. SCC provides an improved description of the binding by including the effects of electronic charge transfer from Zn to O.

We calculate the optimal length and twist of a ZnO nanowire 8.53 Å in radius extending
along the [0001] direction, Fig. 4(a). The wire contains a centered axial screw dislocation, with the 5.4 Å minimum Burger’s vector allowable in ZnO. The simulation cell contains 108 atoms, the same as in the minimum translational cell of the wire, Fig. 4(b). As before, we require a tolerance of $10^{-10}$ Hartree, and the numerical Ewald parameters used are listed in Table I. The increased number of integration nodes required for the 0° case stems from the increased importance of the finite-$l$ terms (here $l_{\text{max}} = 1$) at small angles. In general, because the integrand of the finite-$l$ terms is more nonlinear, more nodes of integration are needed.

The simulations start with relaxed configurations previously obtained with non-SCC-DFTB, or SCC results geometrically twisted to predict a configuration at a new angle (e.g. applying ideal geometric twist to the the simulation result at 1° to begin the 2° simulation). Each conjugate-gradient relaxation took several hours (less than 10) on a single core.

The net charges on the Zn and O atoms range $\pm 0.432-0.575$ e. The total energy difference due to the introduction of SCC corrections is +1.07 Hartree for the 108-atom unit cell. Our previous, non-SCC study of this structure predicted a twist angle of 6.71°/cell and a length of 5.32 Å/cell [48]. The introduction of SCC changes these values to 6.61°/cell and 5.28 Å/cell, respectively, Fig. 4(c).

C. DNA Strand

Finally, we demonstrate the method for simulating heteronuclear biomolecules, when $\theta$ is large and $r \neq r'$ is possible. Here, a larger number of atomic species is present and both the electrostatic and van der Waals sums are needed simultaneously.

Biomolecules are perhaps the most obvious application for objective MD coupled with SCC-DFTB and dispersion. They often possess helical symmetry, and are almost universally characterized by dispersion interactions. All biomolecules are heteronuclear, requiring the consideration of charge transfer for the most accurate description possible. Here we focus on ideal DNA.

Traditionally, DNA is simulated using either cluster approximations or periodic boundary conditions with the particle mesh Ewald method [50, 51]. Both of these methods can be problematic. Cluster simulations may introduce spurious end effects, and make the treatment of long strands of DNA computationally intensive. PBC overcomes these issues, but
TABLE I: SCC-DFTB calculations under objective boundary conditions. Numerical parameters required to reach a tolerance of $10^{-10}$ Hartree in helical Ewald summation of different structures and configurations considered. In order: Ewald split parameter $\eta$, maximum short-range summation index $\zeta_{\text{max}}$, maximum long-range summation indices $l_{\text{max}}$ and $k_{\text{max}}$, and number of nodes $n$ used for numerical integration of $V^L$. Number of k-points required for energy convergence also listed. Actual parameters used listed first, bare minimum parameters required to reach required tolerance listed in parentheses.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\eta$ (Bohr$^{-2}$)</th>
<th>$\zeta_{\text{max}}$</th>
<th>$l_{\text{max}}$</th>
<th>$k_{\text{max}}$</th>
<th>$n$</th>
<th>k-points</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4,2) BN nanotube</td>
<td>$5 \times 10^{-5}$</td>
<td>500(200)</td>
<td>1(0)</td>
<td>1(0)</td>
<td>100(&lt;50)</td>
<td>20(10)</td>
</tr>
<tr>
<td>ZnO nanowire:</td>
<td>$5 \times 10^{-5}$</td>
<td>100(&lt;50)</td>
<td>2(1)</td>
<td>1(0)</td>
<td>100(&lt;50)</td>
<td>10(5)</td>
</tr>
<tr>
<td>$\theta \geq 1^\circ$</td>
<td>$5 \times 10^{-5}$</td>
<td>100(&lt;50)</td>
<td>2(1)</td>
<td>1(0)</td>
<td>100(&lt;50)</td>
<td>10(5)</td>
</tr>
<tr>
<td>$\theta = 0^\circ$</td>
<td>$5 \times 10^{-5}$</td>
<td>100(&lt;50)</td>
<td>2(1)</td>
<td>1(0)</td>
<td>1000(500)</td>
<td>10(5)</td>
</tr>
<tr>
<td>DNA:</td>
<td>$5 \times 10^{-5}$</td>
<td>200(100)</td>
<td>1(0)</td>
<td>1(0)</td>
<td>100(50)</td>
<td>10(5)</td>
</tr>
<tr>
<td>$V$</td>
<td>$5 \times 10^{-5}$</td>
<td>100(50)</td>
<td>1(0)</td>
<td>1(0)</td>
<td>100(50)</td>
<td>10(5)</td>
</tr>
<tr>
<td>$W$</td>
<td>$5 \times 10^{-5}$</td>
<td>100(50)</td>
<td>1(0)</td>
<td>1(0)</td>
<td>100(50)</td>
<td>10(5)</td>
</tr>
</tbody>
</table>

imposes translational symmetry constraints on the structure. Additionally, the number of atoms in the PBC cell is large and quantum treatments becomes less applicable. For this reason, simulations of DNA are typically carried out using empirical force-field models [51].

The objective method carries none of these drawbacks. Segments of arbitrary length may be simulated as part of an infinite helix possessing arbitrary twist, allowing for study of sequence-dependent or general properties without end effects. Additionally, the objective simulations cells typically contain a small number of atoms, permitting the application of SCC-DFTB, which offers superior description of the interatomic interactions.

We have carried out successfully a series of calculations on a DNA molecule - a single helix comprised of adenosine nucleotides, Fig. 5(a). The computational cell contains 33 atoms and comprises a single nucleotide, Fig. 5(b). Because DNA is a soft structure with many possible metastable configurations [51], we focus our demonstration on the determination of the optimal twist angle at a fixed $T = 3.38$ Å. This is the typical value for the DNA B-type
FIG. 5: SCC-DFTB determination of optimal twist of a DNA molecule with $T = 3.38$ Å. (a) Relaxed atomic structure and (b) objective computational domain. (c) Minimization of the strain energy with respect to twist angle, showing optimal twist of $33.27^\circ$/cell. Quadratic curve is fitted only to the four points nearest to the minimum. The torsional stiffness is $0.329$ Hartree Å.

double helix, which was used as the starting configuration for our single-helix simulation. The coordinates used are the default coordinates generated for the B-helix by the nab language [52–54]. Formerly, in order to apply PBC to a DNA structure, investigators had to impose the constraint that there must be an integer number of nucleotides within one or a few 360-degree turns of the helix. This artificial constraint runs contrary to the highly flexible and variable nature of the DNA configuration, and is not present here. The twist per single nucleotide is arbitrary and may represent a structure that possesses no translational periodicity whatsoever.

The interatomic interactions involving elements P, O, N, C, H were described with the mio-1-1 set [3, 55]. We continue to require an accuracy of $10^{-10}$ Hartree, and the values for both the $V$ and $W$ sums are shown in Table I. The simulations take several hours (less than 5) on a single core. We find an optimal twist of $33.27^\circ$/cell, Fig. 5(c). Thus, our simulation predicts that the single helix differs significantly from the $36^\circ$/cell twist angle typically associated with the B-double helix. Our optimized structure does not possess translational periodicity over any reasonable length. The behavior deviates significantly from linear elastic in the angle range we studied. This is expected of when such a soft
material with a complicated configuration space is placed under large strain. Thus, the quadratic fitting is restricted to the four points closest to the minimum. The torsional stiffness is 0.329 Hartree Å. The P atom is the most positively charged at 1.23 e, while the O atoms carry varying negative charges as high as -0.62 e. The other atoms are all closer to neutral. The total dispersion energy is +0.14 Hartree for the 33-atom cell, while the total energy difference due to SCC corrections (not including dispersion) is +0.15 Hartree.

IV. CONCLUSIONS

In this paper, we demonstrated that the generalization of the Ewald method to a helical geometry gives numerical tractable formulas for both the electrostatic potential and van der Waals energies. The approach provides an elegant and robust way to incorporate helical symmetry into self-consistent treatments of the interatomic interactions, including SCC-DFTB. we successfully conducted SCC-DFTB under objective bounder conditions in heteronuclear nano- and bio-structures with various levels of complexity. Overall, objective MD benefits immensely from the coupling with SCC-DFTB as it increases the number and variety of objective structures which can be simulated accurately.

V. ACKNOWLEDGMENTS

We acknowledge useful discussions with M. Elstner, B. Woiczikowski, and A. Enyashin. Computations were performed at the Minnesota Supercomputing Institute.

VI. SUPPLEMENTARY INFORMATION

Fortran code for evaluation the Ewald summation on a helix. Fortran subroutines for the required special functions are freely available as part of the SLATEC Common Mathematical Library on the Netlib Repository. The upper incomplete gamma function is implemented in the short-range potential using the _dgamit.f_ subroutine which computes Tricomi’s incomplete gamma function (Gautschi, Walter. *The incomplete gamma functions since Tricomi*. In *Tricomi’s Ideas and Contemporary Applied Mathematics*, Atti dei Convegni Lincei, n. 147, Accademia Nazionale dei Lincei. 1998.) The long-range potential is calculated using
zbesi.f, which calculates a series of modified Bessel functions of the first kind, of arbitrary orders in integer increment - very convenient for calculating this term for all considered values of \( l \) at once. All the dependencies of these functions are included in SLATEC as well. The machine constant subroutines \texttt{d1mach.f} and \texttt{i1mach.f} need to have the correct lines uncommented to match the machine being used, or the subroutines need to be replaced with modern, self-adapting versions.