Static dielectric response and Born effective charge of BN nanotubes from \textit{ab initio} finite electric field calculations

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\textit{Ab initio} investigations of the full static dielectric response and Born effective charge of BN nanotubes (BN-NTs) have been performed for the first time using finite electric field method. It is found that the ionic contribution to the static dielectric response of BN-NTs is substantial and also that a pronounced chirality-dependent oscillation is superimposed on the otherwise linear relation between the longitudinal electric polarizability and the tube diameter ($D$), as for a thin dielectric cylindrical shell. In contrast, the transverse dielectric response of the BN-NTs resembles the behavior of a thin (non-ideal) conducting cylindrical shell of a diameter of $D + 4\AA$, with a screening factor of 2 for the inner electric field. The medium principal component $Z_\parallel$ of the Born effective charge corresponding to the transverse atomic displacement tangential to the BN-NT surface, has a pronounced $D$-dependence (but independent of chirality), while the large longitudinal component $Z_\perp$ exhibits a clear chirality dependence (but nearly $D$-independent), suggesting a powerful way to characterize the diameter and chirality of a BN-NT.

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\section{I. INTRODUCTION} Since the discovery of carbon nanotubes (CNTs) in 1991\cite{1}, carbon and other nanotubes have attracted considerable interest worldwide because of their unusual properties and great potentials for technological applications. For example, semiconducting CNTs could function as nanoscale field-effect transistors\cite{2}. It was also predicted that nanotori formed from metallic CNTs may exhibit giant paramagnetic moments\cite{2}. Though CNTs continue to attract great interest, other nanotubes such as BN nanotubes (BN-NTs)\cite{4} are interesting in their own right and may offer different possibilities for technological applications that CNTs cannot provide. In particular, as far as the optical and opto-electronic applications of nanotubes are concerned, BN-NTs could be superior to CNTs because BN-NTs are uniformly insulating, independent of their chirality\cite{4}. Furthermore, recent experiments indicate that BN-NTs exhibit stronger resistance to oxidation at high temperatures than CNTs\cite{5}.

Therefore, the properties of both single-walled and multiwalled BN-NTs have been intensively studied experimentally and theoretically in recent years. In this paper, we focus on the dielectric response, including static dielectric constant, electric polarizability and Born effective charge, of BN-NTs. A detailed knowledge of dielectric response is needed, e.g., to characterize optical excitations, screening at contacts, and plasmons in nanotube arrays. Variations in size and chirality may or may not affect dielectric properties, which in turn may be exploited to align nanotubes during, e.g., plasma-enhanced chemical vapor position synthesis\cite{7,8} and to separate different tubes in solutions\cite{2}. Synthesis and separation of specific nanotubes remain an important challenge.

Previously, the static dielectric constant and electric polarizability of nanotubes were typically obtained as the zero frequency limit of the optical conductivity (see, e.g., Refs. \cite{10,11} and references therein), which is calculated using either semiempirical tight-binding method or \textit{ab initio} local density approximation (LDA) or generalized gradient approximation (GGA) within independent particle linear response theory (IPLRT). In this way, only the electronic contribution to the static dielectric constant ($\epsilon_{\infty}$) is calculated\cite{10,11,12,13}. Furthermore, local field effects, which can be substantial for the electric field applied perpendicular to the tube axis\cite{12}, are neglected\cite{10,11}.

Here, we apply the latest finite field electric-enthalpy theory\cite{14,15} to study the static dielectric properties of BN-NTs. This theory allows us not only to obtain the full dielectric constants including both electronic and ionic contributions but also to include the local field effects. Furthermore, also using this theory, we perform the first systematic study of the Born effective charge of the BN-NTs. A knowledge of the dependence of Born effective charge on the diameter and chirality of the nanotubes not only is important to understand their dynamical properties but also would allow us to characterize the nanotubes using, e.g., Raman and infrared spectroscopies.

\section{II. THEORY AND COMPUTATIONAL DETAILS} We use the latest finite field electric-enthalpy theory\cite{14,15} to calculate field-induced electric polarization $P$ and atomic forces $F$. For a small finite field $E$, the dielectric constant is $\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\chi_{\alpha\beta}$ where
\[ \chi_{\alpha\beta} = P_{\alpha}/E_{\beta}. \]

If the atoms are kept fixed, this yields the electronic contribution \( \epsilon_\infty \) (so-called clamped ion dielectric constant) and if both the electrons and atoms are allowed to relax in response to the field, the full static dielectric constant \( \epsilon_{\text{static}} \) is obtained. The electric polarizability \( \alpha \) is given by \( \epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\alpha_{\alpha\beta}/\Omega \) where \( \Omega \) is the unit cell volume. The Born effective charge on the \( j \)th atom is \( e_{\text{th}}^{\alpha\beta} = F_{\alpha\beta}/E_\alpha \). Traditionally, the Born effective charge is obtained via \( e_{\text{th}}^{\alpha\beta} = \Omega (\partial P_\alpha/\partial u_{\alpha\beta})|_{E=0} \)

where \( u_j \) is the displacement of the \( j \)th atom due to the optical phonon mode, and is usually calculated by the finite difference approach. Therefore, the finite field calculations have an advantage of being simple and less CPU-time consuming especially for complex systems like BN-NTs.

We consider a number of representative BN-NTs with a range of diameters from all three types of BN-NTs, namely, the zigzag [(\( n,0 \)], \( n = 5, 6, 8, 12, 16 \)], armchair [(\( n,n \)], \( n = 3, 4, 6, 8, 12 \)], and chiral (4,2), (5,2) BN-NTs. For comparison, we also study the dielectric properties of bulk BN in the cubic, wurtzite and hexagonal structures (denoted as c-BN, w-BN and h-BN, respectively) as well as a single honeycomb BN sheet. Our \textit{ab initio} calculations were performed using accurate projector augmented-wave (PAW) method\(^{16}\), as implemented in the QMAS (Quantum MATerials Simulator) package\(^{17}\).

A supercell geometry was adopted so that the nanotubes are aligned in a square array with the closest interwallal distance between adjacent nanotubes being 9 Å. The isolated BN sheet is simulated by a slab-supercell approach with an inter-shelet distance of 15 Å. A plane-wave cut-off of 35 Ry was used throughout. For BN-NTs, a \( 2 \times 2 \times n \) mesh in the first Brillouin zone is used throughout. For the achiral nanotubes, \( n = 8 \) and for the chiral nanotubes, \( n = 6 \). The ideal nanotubes were first constructed by rolling-up a honeycomb BN sheet. Their atomic positions and lattice constants were then fully relaxed until all the atomic forces and the stress were less than \( 4.0 \times 10^{-5} \) Ry/Bohr and \( 1.0 \times 10^{-6} \) Ry/Bohr\(^{4}\), respectively. The same force and stress convergence criteria were used in the finite-field calculations. The small finite-field used is 0.001 atomic unit\(^{15}\). The calculated field-induced polarization and Born effective charge for the field perpendicular to the tube axis were checked with the usual saw-tooth potential method which cannot be applied for the field parallel to the tube axis, and the results from both approaches agree with each other very well (up to the third digit). Note that the unit cell volume \( \Omega \) is not well defined for nanotubes and the single BN sheet. Therefore, like the previous calculations\(^{4,18}\), we used an effective unit cell volume of the nanotubes and the BN sheet rather than the volume of the supercells which is arbitrary. The effective unit cell volume for a nanotube and the BN sheet is given, respectively, by \( \Omega = \pi DdT \) and by \( \Omega = Ad \)

where \( d \) is the thickness of the BN sheet which is set to the interlayer distance of h-BN. \( D \) and \( T \) are the diameter and length of translational vector of the nanotube\(^{15}\), respectively. \( A \) is the area of the surface unit cell of the BN sheet. Furthermore, in the supercell approach to a single wire (an isolated slab), the periodic dipole images can give rise to a substantial depolarization field which not only affect the transverse component of the field-induced properties but also decrease rather slowly as the supercell dimension increases\(^{18}\).

Therefore, the transverse dielectric constant, electric polarizability and Born effective charges presented below, have been corrected for this artificial depolarization field via one-dimensional Clausius-Mossotti relation\(^{19}\) for the single BN sheet and two-dimensional Clausius-Mossotti relation\(^{18}\) for the BN-NTs. We have checked numerically that the transverse component of these physical properties are independent of the supercell dimension used (within 1\%) for the single BN sheet and also the (5,0) BN-NT.

### III. RESULTS AND DISCUSSION

#### A. Bulk BN structures and single BN sheet

The results for the bulk BN structures which are summarized in Table I. All the theoretical lattice constants of all bulk BN structures agree rather well (within 1.5\%) with the experimental values (see Table I), except \( c \) of h-BN which is 3.3\% smaller than the experimental value. Interestingly, the static dielectric constants and Born effective charges of c-BN and w-BN are very similar, and the anisotropy for w-BN is rather small (Table I). This is due to the fact that although the layer stacking along the \( c \) direction of the wurtzite structure and the one along [111] direction of zincblende structure are different, the local tetrahedral atomic configuration is common to both structures. The calculated dielectric properties for c-BN and w-BN agree rather well (within 4.0\%) with the available experimental values (see Table I). In con-
FIG. 1: (Color online) (a) Atomic arrangement of a single BN sheet and (b) Schematic illustration of the mode of deformation of BN sheet under the in-plane electric field. Note that the magnitude of deformation is exaggerated.

Contrast to w-BN, the anisotropy in the dielectric properties of h-BN is rather pronounced. For example, the Born effective charge for the field along the c-axis ($Z_c$) is only about 1/3 of that for the field perpendicular to the c-axis ($Z_{a(b)}$) due to weak covalency along the c-axis. Here $a$ denotes one of the two in-plane primitive vectors (i.e., the vector connecting the two nearest neighboring B(N) atoms) and $b$ is the vector that is perpendicular to $a$.

It is interesting to compare the last two columns (h-BN and BN sheet) in Table I. As h-BN is a one-dimensional stacking of BN sheets with rather large separation between neighboring sheets, it is natural to expect that both systems may have similar in-plane properties, as is actually seen in Table I except the static dielectric constant. While there is no in-plane anisotropy for the clamped ion dielectric constant and Born effective charge for both h-BN and BN sheet, only the static dielectric constant of BN-NT shows strong in-plane anisotropy. The reason for this is that lattice strain is induced in a BN sheet under the in-plane electric field. The mode of strain is schematically shown in Fig. 1, where the magnitude of strain is much exaggerated. The strain mode is clearly anisotropic with respect to the direction of electric field and induces the anisotropy in the in-plane static dielectric constant for BN sheet. However, such a lattice strain cannot be induced in h-BN because of the alternating array of B and N along the c-axis. The B and N arrangement of a given sheet is reversed in the neighboring sheets so that the strain induced by electric field in the neighboring BN sheets cancels out.

B. BN-NT

1. Longitudinal dielectric constant and electric polarizability

The calculated static dielectric polarizability $\alpha_{zz}$ and dielectric constant $\varepsilon_{static}$ of the BN-NTs are plotted as a function of diameter ($D$) in Figs. 2 and 3, respectively. Fig. 2(a) shows that on average, both the full and clamped ion (electronic contribution only) polarizabilities $\alpha_{zz}$ per unit length for the electric field parallel to the tube axis ($E \parallel \hat{z}$) is roughly proportional to the tube diameter, i.e., $\alpha = aD$, resembling the behavior of a thin dielectric cylindrical shell. This behavior is in strong contrast with the latest finding of $\alpha_{zz} \sim D^2 + C$ for the CNTs from the density-functional perturbation theory (DFPT) calculations$^{18}$ and also with the recent finding of from the IPLRT calculations$^{10}$. Because the number of atoms on a BN-NT per unit length is proportional to $D$, this result indicates that every atom on the BN-NTs has nearly the same static polarizability, as would be the case for insulators. The slope of $\alpha_{zz}$ is $a_z$. 

FIG. 2: (Color online) (a) Longitudinal ($\alpha_{zz}$) and (b) transverse ($\alpha_{xx}$) polarizabilities of BN-NTs as a function of tube diameter ($D$). The dashed lines in (a) are the straight lines fitted to the calculated polarizabilities (symbols), and in (b) are the function of $b(D + \delta)^2$ fitted to the calculated values.
\( \alpha = 4.57 \, \text{Å} \) and \( a_{z,0} = 3.08 \, \text{Å} \) for the full and clamped ion polarizabilities, respectively. Note that the slope \( a_{z,0} \) is nearly identical to the previous IPLRT calculations \((3.04 \, \text{Å}^{3}, 3.13^{13})\) indicating that local field effects for \( E \parallel \hat{z} \) are indeed negligible. However, when the ionic contribution is included, as in the present calculations, the electric polarizability \( \alpha_{zz} \) is significantly increased, by \( \sim 50 \% \), demonstrating the importance of the ionic contribution.

There is clear chirality dependence in \( \alpha_{zz} \) and \( \varepsilon_{zz} \), as shown in Fig. 2(a) and Fig. 3. We first discuss the clamped ion dielectric constants which are denoted by inverse triangles in Fig. 3 to simplify the problem. For a given diameter of BN-NT, zigzag BN-NTs have larger dielectric constant than armchair ones and the chiral ones are intermediate. The chirality dependence is strong for smaller diameters and tends to vanish as the diameter increases. The longitudinal dielectric constant of clamped ion case clearly converges to 4.7 which is the clamped ion dielectric constant of a single BN sheet, which is expected to be the case. The strong chirality dependence of clamped-ion longitudinal dielectric constant comes from the chirality dependence of the band gap. It was reported in Ref. \([11]\) that the band gap of the zigzag BN-NTs would be reduced substantially as the tube diameter decreases, while that of the armchair BN-NTs depends on the diameter only slightly. It is known that the systems with a smaller band gap would have a larger dielectric constant. For static longitudinal dielectric constant, the present calculation takes account of only the relaxation of atomic positions with a fixed unit cell. Due to the difficulty in practical calculations, the shear deformation of the unit cell as observed in a single BN sheet (Fig. 1) is not taken into account. Therefore the behavior of the static longitudinal dielectric constant shown by triangles in Fig. 2 is basically the same as those of clamped ion case. The large diameter limit of static dielectric constant is about 6.4 which is close to the value for a single BN sheet obtained within the same constraint of atomic relaxation.

2. Transverse dielectric constant and electric polarizability

We begin our discussion with rather simple features. First, the transverse quantities (in Fig. 2(b) and Fig. 3) do not show appreciable chirality dependence for the whole range of diameter. Second, the ionic contribution is rather small, being only \( \sim 15 \% \) of the electronic contribution in the polarizability [Fig. 2(b)]. Third, the large diameter limit of transverse dielectric constant may be given by the circular average of the response of each part of the BN-NT surface, which may be approximated by \( 0.5(\varepsilon_{\text{static}}^{aa,bb} + \varepsilon_{\text{static}}^{bb,aa}) \) with quantities for a single BN sheet. As we do not take account of the shear strain for BN-NT, \( \varepsilon_{\text{static}}^{aa,bb} \) is about 6.4 and the converged value of the squares (in Fig. 3) in the large diameter limit may be about 4.0. The most surprising fact in the transverse quantities is that the transverse polarizability \( \alpha_{xx} \) in Fig. 2(b) exhibits a rather different behavior\([11,13]\). In fact, \( \alpha_{xx}(D) \) can be nicely fitted to \( \alpha_{xx} = b(D + \delta)^2 \), as can be seen from Fig. 2(b). This indicates that as far as the transverse dielectric properties are concerned, a BN-NT behaves like a thin (nonideal) conducting cylindrical shell\([22]\) (or a system of electrons moving freely on a cylindrical shell\([22]\)) with an effective diameter of \( D + \delta \). The parameters \( b \) and \( \delta \) obtained by the fitting are, respectively, 0.0629 and 4.13 for the full polarizability, and 0.0523 and 4.40 for the clamped ion polarizability. \( \delta \) is slightly larger than the effective thickness \( (d \sim 3.3 \, \text{Å}) \) of the BN sheet mentioned above. The screening factor of the inner electric field \( \varepsilon_{\text{in}} \) by a BN-NT is \( \varepsilon_{\text{out}}/\varepsilon_{\text{in}} = 1/(1 - 8b) \approx 2 \) \( (\varepsilon_{\text{out}} \) is the applied field outside the BN-NT) when the full response of the BN-NT is considered. Note that for a long classical dielectric cylindrical shell, the inner electric field \( \varepsilon_{\text{in}} \) is also uniform and along \( \varepsilon_{\text{out}} \). However, \( \varepsilon_{\text{in}} = 4\varepsilon_{\text{out}}\varepsilon/\varepsilon (\varepsilon + 1)^2 = (\varepsilon - 1)^2(D + d)^2/(D - d)^2 \) would be enhanced rather than screened. For example, for the \((8,8)\) BN-NT, the screening factor is 0.4 if \( \varepsilon_{\text{static}} = 2.58 \) [for the \((8,8)\) BN-NT] is used or 0.8 if \( \varepsilon_{\text{static}} = 1.65 \) [for the BN sheet] is used. To see whether this phenomenological interpretation in terms of a thin conducting cylindrical shell is an accidental coincidence or not, we plot the calculated electric potential on a plane perpendicular to the tube axis of the \((8,8)\) BN-NT in Fig. 4(a) and also calculate the total electric field along the applied electric field line going through the center of the BN-NT [Fig. 4(b)]. Fig. 4 clearly shows that the electric field inside the BN-NT is indeed uniform and considerably reduced. The screening factor from Fig. 4(b) is 2.08 but not infinite as would be expected from a perfect conducting cylindrical shell. We also plot the electric field for some other BN-NTs and find the same situation. Note that both the metallic and semiconducting CNTs exhibit the
The transverse polarizability from the present study exhibits a pronounced monotonic dependence on the tube diameter (but independent of chirality) while the small component ($Z'_z$) is almost a constant. In contrast, the large component ($Z'_x$) shows a clear chirality dependent oscillation superimposed on the mean value of 2.70 e (the in-plane components of the Born effective charge of the single BN sheet) (see Fig. 5 and Table I). These interesting diameter-dependence of $Z'_x$ and chirality-dependence of $Z'_z$ suggest that one could determine both the diameter and chirality of a BN-NT by measuring its Born effective charges using, e.g., Raman and infrared spectroscopies. Characterization of the chirality and diemeter of a BN-NT is still a great challenge.

Interestingly, as the tube diameter becomes large, $Z'_x$ and $Z'_y$ tend to approach to the $Z'_x$ and $Z'_y$ components of the Born effective charge of the single BN sheet for the field perpendicular and parallel to the sheet plane (Table I), respectively. This is perhaps not surprising because the observed monotonic diameter dependence of the $Z'_x$ and $Z'_z$ merely reflect the degree of the local curvature of the BN-NTs with a finite diameter.

**IV. CONCLUDING REMARKS**

To summarize, we have carried out a systematic ab initio study of the static dielectric properties of the BN-NTs within density functional theory with the LDA plus the latest finite-field electric-enthalpy theory. Specifically, the full static dielectric constant, electric polarizability and Born effective charges of a number of BN-NTs as well as the single graphitic BN sheet and bulk BN structures have been calculated. The calculated lattice constants, dielectric constants and Born effective charges for the bulk BN structures are in good agreement with available experiments. We find that the ionic contribution to the static dielectric response of BN nanotubes (BN-NTs) is substantial and that a clear chirality-dependent oscillation is imposed on a linear relation between the longitudinal electric polarizability and the tube diameter, as for a thin dielectric cylindrical shell. We also find that the calculated features of the transverse dielectric response of the BN-NTs resemble that of a thin conducting cylindrical shell, with a screening factor of 2 for the inner electric field. Our calculations also show that for each BN-NT, the medium principal component of Born effective charge tensor has a pronounced dependence on diameter (but independent on chirality) and the large principal component exhibits a chirality dependence (but nearly independent
on diameter), suggesting that a BN-NT could be characterized by measuring its Born effective charges using, e.g., Raman and infrared spectroscopies.

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