

Soft Matter

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Geometrically nonlinear deformation and the emergent behavior of polarons in soft matter

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Mechanical strain can alter the electronic structure of both bulk semiconductors as well as nano structures such as quantum dots. This fact has been extensively researched and exploited for tailoring electronic properties. The strain mediated interaction between the charge carriers and the lattice is interpreted through the so-called deformation potential. In the case of soft materials or nano structures, such as the DNA, the deformation potential leads to formation of polarons which largely determine the electronic characteristics of the DNA and similar polymer entities. In addition, polarons are also speculated to be responsible for the mechanism of quantum actuation in carbon nanotubes. The deformation potential is usually taken to be a *linear* function of the lattice deformation ($U \sim \alpha \epsilon$) where α is the deformation potential “constant” that determines the coupling strength and ϵ is the mechanical strain. In this letter, carefully accounting for nonlinear geometric deformation that has been hitherto ignored so far in this context, we show that the deformation potential *constant* is renormalized in a non-trivial manner and is hardly a *constant*. It varies spatially within the material and with the size of the material. This effect, while negligible for hard materials, emerges to be important for soft materials and critically impacts the interpretation of quantities such as polaron size, binding energy, and accordingly, electronic behavior.

Mechanical strain is well-known to impact the electronic structure and hence the optoelectronic properties of both bulk semiconductors as well as, in even more unusual ways, nano structures like quantum dots^{1–5}. A rich body of literature exists that have explored this coupling and indeed strain is now routinely used to tailor the band gap, mobility of charge carriers and other aspects of the electronic structure^{6–9}. Although inorganic semiconductors have been heavily studied in this context, the topic of strain-electronic structure coupling is also of importance for organic semiconductors which offer some advantages—such as being lighter, flexible and more economical. Organic semiconductors are increasingly being considered for applications in electronic devices like light emitting diodes¹⁰, field effect transistors^{11,12} among others^{13–15}. In this letter, our focus is on the concept of “polaron”^{17,18} which plays a central role in the charge transport mechanism in the DNA^{19–22} and other organic polymers^{23–26}. We also note that the study of polaron is of interest due to several tantalizing basic science questions associated with this topic not to mention the recently discussed ramifications in superconductors^{27–29} and quantum actuation mechanism in carbon nanotubes (CNTs)^{30–32}. DNA is a one dimensional (1D) prototypical soft nanoscale material whose electronic properties

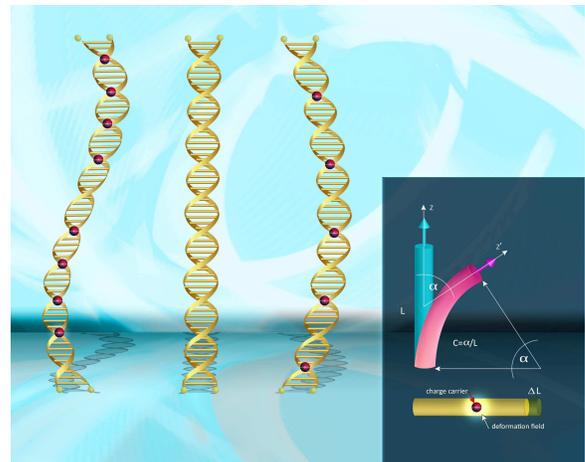


Fig. 1 The figure schematically illustrates how an extra charge carrier may form the quasi-particle called polaron and induce different deformation modes such as extension/contraction, bending, twisting in the DNA or similar 1-D nano structures.

(including conduction) are dictated by that of polaron motion. Accordingly, throughout this communication, we will frequently refer to the DNA to highlight the key message(s) of our work although the implications of our work are broadly applicable to soft matter in general.

The polaron, in brief, is a type of quasiparticle which forms due to the interaction between charge carriers (electron or hole) and phonons. In the present context, where the discussion is on

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strain-mediated changes in electronic structure, the interaction is between charge carriers and *acoustic* phonons. By definition, the acoustic polaron is a quasiparticle that is a result of a charge carrier trapped by the self-induced localized lattice distortion (see Fig. 1).^{*} More colloquially, the polaron may be understood to be a charge carrier surrounded by a “cloud” of strain. For small enough nano structures (e.g. carbon nanotubes, quantum dots) or soft materials, injecting a charge carrier may form a polaron. As schematically depicted in Fig. 1, any stimuli that interacts with the charge carrier will then disturb the surrounding strain field and hence cause deformation—leading to the so-called quantum actuation mechanism.

Despite significant work to date, several controversies still remain regarding the fundamental mechanisms underpinning charge transport in DNA and similar soft structures^{34–41}. A well-accepted (although still debated) charge transport mechanism is the formation of the so-called “large”[†] polaron. In this notion, the charge carrier spreads over several bases or lattice sites and is “dressed” by the lattice distortion in order to minimize the energy¹⁹. In particular, in a long line of pioneering work predicated on polaron motion, Conwell and co-workers have clarified several key aspects of charge transport mechanisms in the DNA^{42–46}. Other related work have examined the stability of polarons in DNA^{47,48} and the effects of environment^{42,44}, electric fields⁴⁹ and temperature^{20,50}.

A key role in the models that purport to describe polarons in organic materials (or for that matter, even inorganic ones) is played by the material property called the electron-phonon coupling or deformation potential *constant*. The electronic transport between the adjacent lattice sites is accompanied by the lattice distortion due to the electron-phonon interaction which results in the polaronic state. In particular, the strength of this coupling strongly affects the polaron size, effective mass and therefore the mobility of charge carriers in soft materials. As already alluded to earlier, this parameter is assumed to a constant value for a given material and its estimation appears to vary significantly depending on which method is used. In this letter, we modify the continuum Holstein based model¹⁷ to correctly account for geometric deformation nonlinearity that is essential in the study of easily deformable soft materials. We show that, instead of a “constant”, the electron-phonon coupling parameter may vary spatially or in the case of the DNA, from site to site and also with the size of the structure. The effect of geometric deformation nonlinearity is found to be the quantum mechanical analog to the electrostatic Maxwell stress effect in soft materials. We present the effect of this aforementioned geometric nonlinearity on the polaron binding energy and polaron induced mechanical deformation in one dimensional nanoscale materials ranging from hard materials like CNTs to soft polymer chains like the DNA.

^{*} Discussion of other types of polarons that pertain, for example, to interactions between charge carriers and optical phonons among others are beyond the scope of this work and will digress from our main theme. The reader is referred to Ref³³ for further information.

[†] If the extension of the polaron is in the order of lattice spacing, it is referred to as “small” and conversely, a large polaron spreads over several lattice sites.

In the following, we outline the mathematical framework to incorporate the effect of geometric deformation nonlinearity on the deformation potential. Our starting point is the continuum Holstein model. The approach couples elasticity with quantum mechanical effects (or electronic structure) in the spirit of the envelope function and **k.p.** approach^{51,52}. We adopt this approach in the interest of transparency and analytical tractability. The chosen approach does not impact the central message of our work. Other formalisms such as the discrete Holstein model¹⁷, Su-Schrieffer-Heeger Hamiltonian¹⁸ and Kohn-Sham Density Functional Theory (DFT) may also be employed but (in our opinion) the key ideas are most clearly presented in the field theoretic formalism outlined below.

Consider an extra charge carrier (electron or hole) introduced into a dielectric body. For simplicity, we neglect the kinetic energy of lattice motion since the time scale dictating the relaxation of the extra charge carrier is sufficiently rapid compared to the atoms and is able to adjust to the instantaneous positions of the atoms⁵³. We also restrict ourself to a non-spin energy calculation throughout this work.

We begin with the postulations that (i) the state of the system is described by the deformation $\chi : \Omega_R \rightarrow \Omega$ and the electronic wave function $\psi : \Omega \rightarrow \mathbb{C}$ associated with the charge carrier, and (ii) the Hamiltonian of the system is given by⁵³:

$$H = \int_{\Omega} \frac{\hbar^2}{2m^*} |\text{grad} \psi|^2 + |\psi|^2 U dv + \int_{\Omega_R} W_{\text{el}} dV, \quad (1)$$

where m^* is the effective mass of the charge carrier and the first term is the kinetic energy, the term U is the deformation potential characterizing the electron-acoustic phonon interaction, and the last term W_{el} is the elastic strain energy density. For the ground state, our problem is to minimize the total Hamiltonian with respect to all admissible wave functions and deformations. In this procedure, we must carefully distinguish two configurations (Ω_R vs. Ω), which would give rise to the *geometric nonlinearities*.

One apparent difficulty in solving the variational problem defined by (1) arises from the fact that the deformed configuration Ω depends on the deformation χ of the body which is coupled to the wave function ψ . A systematic way to address this difficulty is to “pull-back” all quantities to the reference configuration. To be precise, let $\Psi(\mathbf{X}) = \psi(\chi(\mathbf{X}))$ be the wave function with respect to the reference configuration, and denote by

$$\mathbf{F} = \nabla \chi, \quad J = \det \mathbf{F} \quad (2)$$

the deformation gradient and the Jacobian. Here and subsequently, we denote by \mathbf{x} (resp. \mathbf{X}) the spatial/Eulerian (resp. material/Lagrangian) coordinates, and by grad/div and $\nabla/\nabla \cdot$ the gradient/divergence operator with respect to \mathbf{x} and \mathbf{X} , respectively. Then by changes of variables $\mathbf{x} \rightarrow \mathbf{X}$, the Hamiltonian (1) can be written as a functional of deformation χ and wave function Ψ :

$$H = \int_{\Omega_R} \left[\frac{\hbar^2 J}{2m^*} |\mathbf{F}^{-1} \nabla \Psi|^2 + JU |\Psi|^2 + W_{\text{el}} \right] dV. \quad (3)$$

The normalization condition for the electronic wave function *in*

the reference configuration can be expressed as:

$$\int_{\Omega} |\Psi|^2 dv = \int_{\Omega_R} J |\Psi|^2 dV = 1. \quad (4)$$

Standard first-variational calculations for the Hamiltonian (3) with the constraint (4), though rather tedious, yield the Euler-Lagrange (EL) equations for determining polaron states (χ, Ψ) that duly account for geometric nonlinearity. However, the governing equations are rather complicated and their physical meaning is somewhat obscure. To render the impact of geometric deformation nonlinearity on the deformation potential more transparent, we introduce the displacement $\mathbf{u} = \chi(\mathbf{X}) - \mathbf{X}$. Let $\nabla \mathbf{u} = \mathbf{F} - \mathbf{I}$ be the (unsymmetrized) strain and $\eta \sim |\nabla \mathbf{u}|$ be the order of magnitude of the strain. For simplicity, the elastic energy density and deformation potential are written as

$$W_{\text{el}} = \frac{1}{2} \nabla \mathbf{u} \cdot \mathbf{C} \nabla \mathbf{u} \quad \text{and} \quad U = \alpha_0 \nabla \cdot \mathbf{u}, \quad (5)$$

respectively, where \mathbf{C} is the fourth-order elasticity tensor and α_0 is the deformation potential constant. Formally, we expand the first two terms in (3) in terms of strain as:

$$\begin{aligned} \frac{\hbar^2 J}{2m^*} |\mathbf{F}^{-1} \nabla \Psi|^2 + JU |\Psi|^2 &= \frac{\hbar^2}{2m^*} |\nabla \Psi|^2 \\ &+ |\Psi|^2 U + |\Psi|^2 \langle \Sigma, \nabla \mathbf{u} \rangle + o(\eta), \end{aligned} \quad (6)$$

where

$$\Sigma = \frac{\hbar^2}{2m^* |\Psi|^2} [|\nabla \Psi|^2 \mathbf{I} - \nabla \Psi^* \otimes \nabla \Psi - \nabla \Psi \otimes \nabla \Psi^*].$$

Neglecting higher order $o(\eta)$ -terms in (6) we rewrite the Hamiltonian (3) in terms of (\mathbf{u}, Ψ) as

$$H = \int_{\Omega_R} \left[\frac{\hbar^2}{2m^*} |\nabla \Psi|^2 + U^{\text{eff}} |\Psi|^2 + W_{\text{el}} \right] dV, \quad (7)$$

where

$$U^{\text{eff}} = U + \langle \Sigma, \nabla \mathbf{u} \rangle. \quad (8)$$

Comparing (7) with (1), we refer to U^{eff} as the *effective* deformation potential. Neglecting $\langle \Sigma, \nabla \mathbf{u} \rangle$ in (8) we obtain the coupled Schrödinger-Elasticity equations for (Ψ, \mathbf{u}) ^{5,30}:

$$\begin{cases} \left[-\frac{\hbar^2}{2m^*} \nabla^2 + \alpha_0 \nabla \cdot \mathbf{u} \right] \Psi = E \Psi, \\ \nabla \cdot (\mathbf{C} \nabla \mathbf{u} + \alpha_0 |\Psi|^2 \mathbf{I}) = 0. \end{cases} \quad (9)$$

From Ref^{19,30} we estimate that $\alpha_0 |\Psi|^2 \sim 0.01\text{-}1 \text{ eV}/\text{\AA}$ in magnitude for one dimensional materials such as carbon nanotube or DNA strands. From (9), we see that for hard materials, the assumption of small strain is indeed an accurate approximation. For instance, the stiffness of carbon nanotubes is approximately $600 \text{ eV}/\text{\AA}$, implying strains η of the order of 10^{-4} . However, for soft macromolecules such as DNA, the stiffness is of the order of $1 \text{ eV}/\text{\AA}$, implying that the strain η can be as large as 10-100%. Indeed, in the latter case, the use of (9) for estimating polaron

states is quite questionable. As will be shown shortly, the geometric deformation nonlinearity significantly alters the wave function, energy, deformation and possibly stability of polaron states for soft materials undergoing large deformations. In particular, the Hamiltonian (7) and constraint (4) imply the following governing equations for (\mathbf{u}, Ψ) :

$$\begin{cases} \left[-\frac{\hbar^2}{2m^*} \nabla^2 + \alpha_0 \nabla \cdot \mathbf{u} \right] \Psi + \mathcal{L}^{\text{gn}} \Psi = E \Psi, \\ \nabla \cdot [\mathbf{C} \nabla \mathbf{u} + \alpha_0 |\Psi|^2 \mathbf{I} + \Sigma^{\text{gn}}] = 0, \end{cases} \quad (10)$$

where \mathcal{L}^{gn} (Σ^{gn}) is the additional operator (stress) arising from the geometric nonlinearity:

$$\mathcal{L}^{\text{gn}} \Psi = \frac{\hbar^2}{2m^*} \nabla \cdot \{ [-(\nabla \cdot \mathbf{u}) \mathbf{I} + \nabla \mathbf{u} + (\nabla \mathbf{u})^T] \nabla \Psi \}, \quad (11)$$

$$\Sigma^{\text{gn}} = (\Sigma - E \mathbf{I}) |\Psi|^2.$$

From (10)₂, we see that it is necessary to consider the leading-order term from geometric nonlinearity if $\frac{\hbar^2}{2m^*} |\nabla \Psi|^2$ is comparable to the elastic stress $\mathbf{C} \nabla \mathbf{u}$ (or $k\varepsilon$ for 1D case). We also remark that the exact nonlinear Euler-Lagrange (governing) equations may be obtained from the original Hamiltonian (3) which must be used if the strain η is large.

From (9) or (10), we see that the equations for polaron states are in general, nonlinear and not amenable to explicit solutions. For 1D materials/structures such as nanotubes and conjugate polymer chains, Ref^{23,30} obtained explicit solutions to (9) by suppressing the degrees of freedom in transverse direction (—these works however ignored the effect geometrically nonlinear deformation). In the following, we explore the effect of geometric nonlinearity. We denote the longitudinal displacement by $u: \mathbb{R} \rightarrow \mathbb{R}$, the normal strain by $\varepsilon = u_{,X}$ and the stretch ratio by $\gamma = 1 + u_{,X}$. Using (5) we write the deformation potential as $U = \alpha_0 \varepsilon$ and strain energy density function $W_{\text{el}} = \frac{1}{2} k \varepsilon^2$. From the *exact* Hamiltonian (3), we find the following simplified Euler-Lagrange equations for 1D polaron states (u, Ψ) that account for geometrically nonlinear deformation:

$$\begin{cases} -\frac{\hbar^2}{2\gamma m^*} \left[\frac{\Psi_{,X}}{\gamma} \right]_{,X} + \alpha_0 u_{,X} \Psi = E \Psi, \\ \left[k u_{,X} + \alpha_0 |\Psi|^2 - \frac{\hbar^2}{2m^*} \left(\frac{\Psi_{,X}}{\gamma} \right)^2 - E |\Psi|^2 \right]_{,X} = 0. \end{cases} \quad (12)$$

Evidently, the last two terms in (12)₂ arise due to the geometric nonlinearity. We let two ends of the material free, therefore the requisite boundary conditions may be written as:

$$\begin{cases} \Psi = 0, \\ k u_{,X} + \alpha_0 |\Psi|^2 - \frac{\hbar^2}{2m^*} \left(\frac{\Psi_{,X}}{\gamma} \right)^2 - E |\Psi|^2 = 0. \end{cases} \quad (13)$$

To solve the two coupled 1D equations (12) subject to boundary conditions (13), we performed an iterative numerical calculation using the so-called “imaginary time method”. The reader is referred to Ref⁵⁴⁻⁵⁶ for further details on the numerical procedure

to solve such classes of boundary value problems. We only briefly summarize the basic idea here. First, a suitable initial guess (e.g. a Gaussian function) is made for Ψ and ε as the starting point for the iteration, and then Ψ and ε were solved in the next iteration using the following relationships:

$$\frac{\partial \Psi(X, \tau)}{\partial \tau} = -\frac{\delta E}{\delta \Psi}, \quad \frac{\partial \gamma}{\partial \tau} = -\frac{\delta E}{\delta \gamma}.$$

We used forward Euler for time discretization and a second-order central finite difference for discretizing the spatial derivatives. The normalization and boundary conditions were also imposed at each step. After several trials, we selected a time step of $\Delta\tau = 0.001$ s and spatial unit $\Delta h = 0.5$ Å. In each iteration, we calculated the total energy—which decreases with increasing number of iterations. Convergence was considered to have been achieved when the energy difference between iterations dropped to less than 10^{-4} eV.

To illustrate how the geometrically nonlinear deformation influences the key polaron properties, we present the results of our calculation of the polaron binding energy and polaron induced strain for a wide range of 1D materials. From the contour plots shown in Fig. 2 and Fig. 3, we observe that the effect of geometrically nonlinear deformation for both the induced strain and the binding energy shows a similar pattern: the effect is minor for hard materials (e.g. carbon nanotubes) and significant for elastically soft materials (e.g. DNA). In particular, for materials that are elastically soft and have a strong electron-phonon coupling constant, the effect is quite large and can dramatically change the two key aforementioned polaron signature properties. In short, the central message of this letter, that is amply justified by the two contour plots, is that geometric nonlinearities cannot be ignored for polarons in soft materials.

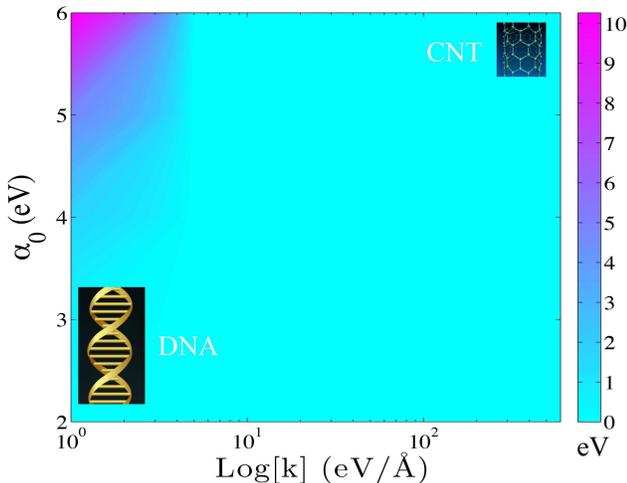


Fig. 2 The contour plot shows the change in polaron binding energy due to the geometric deformation nonlinearity. For simplicity, we have fixed the value of $\frac{\hbar^2}{2m^*} = 2.312$ eVÅ² and varied α_0 and k in the range $1 \leq \alpha \leq 10$ eV and $1 \leq k \leq 700$ eV/Å

To study the effect of effective mass, we fixed the stiffness constant k to be 15 eV/Å and varied both the effective mass

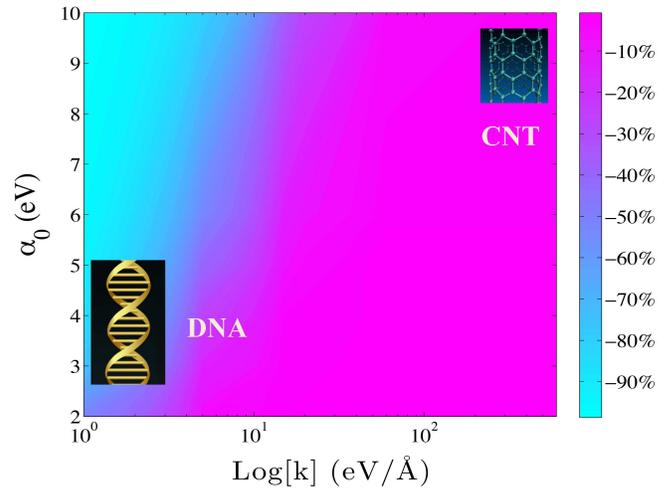


Fig. 3 The contour plot indicates how the geometric nonlinearity plays a role in polaron-induced strain depending on the elastic and electron-phonon properties of the materials. As in Fig. 2, we have fixed the value of $\frac{\hbar^2}{2m^*}$ and varied the values of α_0 and k within the same range.

and coupling constant. For simplicity, we only performed calculations for three different values of the effective mass (e.g. $\frac{\hbar^2}{2m^*} = 2.312; 8.1; 16.94$ eV Å²) which cover the range of typical values in materials from DNA to carbon nanotubes. The overall trend is found to be the same as shown in Fig. 4. Through this analysis, we can see that as the charge carrier becomes heavier, the geometric nonlinear effect becomes larger. This is due to the fact that as the charge carrier becomes heavier, it “feels” the potential in a stronger way and gets trapped in deeper energy wells with larger deformations around it. As shown before, the geometric nonlinear effect on binding energy increases with respect to the increasing coupling constant.

To confirm the intuitive assertion that the aforementioned effect ought to be negligible for hard materials, we compare a CNT with DNA. For the CNT(11,0) case, we use the same parameters, $\alpha_0 = -8.9$ eV and $k = 644$ eV/Å, as in Ref³⁰. The electron (hole) effective mass can be written in terms of hopping integral t_0 as:

$$m^* = \frac{\hbar^2}{2t_0 a^2} \quad (14)$$

where a is the lattice constant (2.46 Å for CNT and 3.4 Å for DNA). The hopping integral for CNT is roughly 2.94 eV. The hopping integral depends on the DNA geometry as well as environment⁵⁷. Both DFT calculations and theoretical methods estimate that the hopping integral is within the range 0.02-0.3 eV.^{19,41,58,59} We select t_0 to be 0.3 eV. As discussed in Ref²³, we have used the corresponding parameters relationship between continuum SSH and Holstein Hamiltonian to reduce the difference between them. Based on that, we selected the electron-phonon coupling constant (α_0) to be 8.16 eV (4×0.6 eV/Å \times 3.4 Å) and the elastic constant k is set to 11.56 eV/Å (4×0.85 eV/Å² \times 3.4Å).

As well evident from Fig. 5, both the polaron probability density distribution and deformation do not change in the case

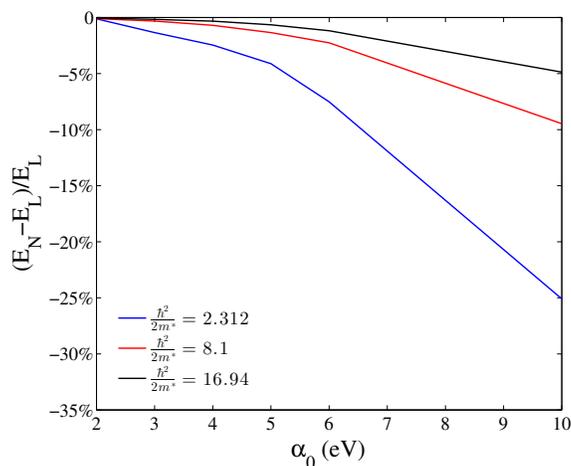


Fig. 4 The figure depicts the interplay between the polaron binding energy and effective mass. The stiffness is kept fixed at $k = 15 \text{ eV/\AA}$. E_N and E_L denote the polaron binding energy both with and without the geometric nonlinear effect, respectively.

of CNT—whether or not deformation nonlinearities are accounted for. The polaron length and the maximum strain is about 44 nm and 1.46×10^{-5} respectively. The binding energy is -2.02×10^{-2} meV. All these values match well with reported ones in past works³⁰. However, a significant effect is well-evident for DNA. The polaron length is increased from 2.41 Å to 3.65 Å. Also, the maximum strain is reduced from -14.7% to -10.7% which corresponds to a total change of length 0.71 Å and 0.66 Å respectively. Furthermore, the binding energy is decreased from -0.2 eV to -0.15 eV. Another finding is that, in the absence of nonlinearity, the binding energy is exactly one-third of the total electronic energy which is consistent with previous work^{53,60}.

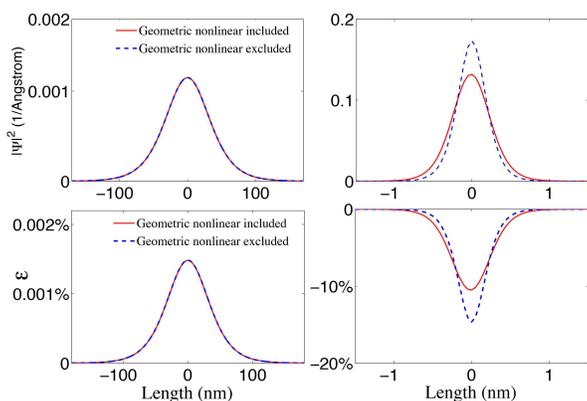


Fig. 5 The figure shows the probability density distribution (top panel) and deformation distribution (bottom panel) along the longitudinal axis of the CNT and DNA. The left panel for the CNT and right panel is for the DNA.

In conclusion, we have shown that contribution of geometrically nonlinear deformation must be properly accounted for when describing polarons in soft materials. In soft materials, an “effec-

tive” deformation potential constant may be defined which is no longer a *constant* and nearly all the significant polaron properties and behavior are dramatically altered—such as the polaron binding energy and polaron-induced deformation. These altered polaron properties are likely to play a central role in charge-transfer mechanisms in soft materials like the DNA and therefore represent an intriguing avenue for further study. We note here that we only considered a single charge carrier (and hence a single polaron). Several of our predictions on the alterations in polaron properties due to nonlinear geometric effects are likely to be even more exaggerated if multiple polarons are considered (non-trivial as such a study may be, however). In the past, many potential applications of the DNA have been proposed, in particular, designing it as an electron-optical device, biosensor and/or nanoactuator^{61,62}. Polaron mediated charge transport may be important for these applications and the extension of the present work for those situations is anticipated. One of the implications of this work is that we can remotely deform a sufficiently soft material by simply exposing it to light. The latter will certainly alter the electronic structure of the soft object (provided it is small enough) and, through mediation by polarons, induce large deformations.

Acknowledgements

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