Magnetization of circular DNA

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We investigate the orbital magnetization of DNA molecules in the relaxed circular structure. It is shown that DNA of homogeneous sequence exhibits paramagnetic responses to external magnetic fields and, surprisingly, the magnetism of circular DNA is equivalent to that of linear DNA. This turns out to result from the fact that the electron population is localized largely on one of the strands. More intriguingly, the magnetic susceptibility is observed to depend on the ring topology defined by the linking number. We also consider sequence heterogeneity and find that the magnetization displays characteristic oscillations, the pattern of which depends crucially on the sequence and the base content.

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The perspective of the molecular usage as nanowires has led to a wide range of experimental as well as theoretical work on the electric properties of DNA molecules. However, the mechanism for the charge transport is still unsettled. Experimentally, it has been found that DNA can be either a good conductor, a semiconductor, or even an insulator [1]. On the other hand, it is known that conducting properties of DNA are easily modified by environment factors such as counterions [2] and hydration [3]. More importantly, conduction amplitudes depend highly on the contact strength between the molecules and electrodes, which should be one of the crucial causes for the diverse experimental results. To circumvent this, indirect measurement of the electronic properties has been carried out in a noncontact way [4], where some intriguing magnetic properties of DNA molecules have been reported. The key finding is that the B-DNA manifests paramagnetic responses to external magnetic fields at extremely low temperatures. Such magnetic properties were interpreted on the analogy between the orbital magnetization with the persistent current [4]; yet there is a question as to the origin, leading to controversy [5,6].

With regard to persistent currents, ring-structured systems have been studied intensively [7,8]. It is noteworthy that DNA in a higher organism forms a loop structure, referred to as circular DNA; when a DNA chain is bent to form a loop but its two ends are disconnected, we regard the geometry as linear, which is topologically equivalent to a straight line. Especially, there exists the so-called relaxed circular DNA, where the base-pair turn accomplishes the desired twist for the circular form, making writhe unnecessary [9]. In a simple-minded picture, its geometry can be considered as the ring of a twisted ladder (see Fig. 1). If the observed magnetization arises from the electronic orbital motion so that its origin is the same as that of the persistent current, the circular structure is expected to display features distinctive from those of the linear structure. A recent theoretical work [10] deals with linear DNA molecules and explains observed paramagnetism, together with its fast decay with temperature and structural dependence [4]. Yet, further investigation of the magnetic properties of circular DNA in comparison with those of linear DNA can provide a direct evidence for unraveling nature of the DNA magnetism.

The present work is to examine theoretically the orbital magnetization of relaxed circular DNA. We thus consider electrons moving on a twisted ladder of a ring geometry in the presence of magnetic fields. Here the two characteristic flux, the magnetic flux through the duplex face and that through the ring, come into play to determine the phase factors of the electron hopping integral [11]. Note that due to the helical twist the unit cell area projected onto the field direction varies along the helix, resulting in a complicated flux distribution. We first address the analytically soluble case of homogeneous sequence, with the twist disregarded. It is shown that for DNA of homogeneous sequence the magnetization is determined solely by the flux through the duplex face, indicating that the magnetism of circular DNA is equivalent to that of linear DNA. This is confirmed by numerical calculation with the helical turn explicitly taken into account. It is also found that the magnetic susceptibility depends on the linking number or the twist angle: the higher the linking number, the smaller the susceptibility. This simply reflects that with the linking number increased, the projected area shrinks, so as to reduce the effective field strength. We then consider the sequence heterogeneity, having in mind the two types of measurements: One is on the single-ring DNA, and the other on an ensemble of them. For the former, we choose a number of different sequences to demonstrate sequence-specific oscillations of the magnetization. For the latter, the issue of the ensemble average arises

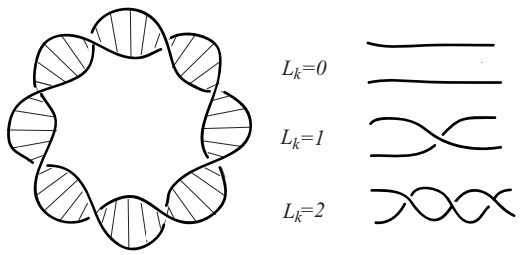

FIG. 1. Schematic diagram of circular DNA: The annulus geometry of the twisted duplex (L_k=4) is shown on the left-hand side whereas displayed on the right-hand side is the area variation according to the linking number.

TABLE I. Tight-binding parameters (in units of eV) used in our calculation, which are the average values of the intrastrand parameters for the various stacking directions in Ref. [12] and the interstrand hopping parameters in Ref. [13].

$(\alpha\beta)$	ϵ_α	$t_\parallel^{(\alpha\beta)}$	$(\alpha\beta)$	$t_\perp^{(\alpha\beta)}$	$t_\parallel^{(\alpha\beta)}$
GG	7.77	0.238	*GC*	0.033	0.510
CC	8.87	0.341	*AT*	0.030	0.320
AA	8.25	0.105	*GA*		0.300
TT	9.13	0.145	*CA*		0.240
GT		0.172	*CT*		0.160

and is discussed extensively in the context of persistent currents. It is known that the current amplitude of a collection of uncorrelated rings with strong disorder is characterized by the root-mean-square current (often referred to as the typical current) [8]. Evoking the close resemblance of the orbital magnetization to the persistent current, we compute the typical magnetization, to find its oscillation amplitude more significant for the molecules having higher contents of guanine and cytosine bases.

We begin with the tight-binding Hamiltonian for spinless fermions: $\mathcal{H}=\mathcal{H}_\perp+\mathcal{H}_\parallel$ with

$$\mathcal{H}_\perp = \sum_{i=1}^{N} [t_\perp^{(\alpha\beta)}|i,\alpha\rangle\langle\widetilde{i,\beta}| + t_\perp^{(\beta\alpha)}|\widetilde{i,\beta}\rangle\langle i,\alpha|],$$

$$\begin{aligned}\mathcal{H}_\parallel = &\sum_{i=1}^{N} [t_\parallel^{(\alpha\beta)} e^{i\mathcal{A}_i}|i,\alpha\rangle\langle i+1,\beta| + \text{H.c.}] \\ &+ \sum_{i=1}^{N} [t_\parallel^{(\alpha\beta)} e^{i\tilde{\mathcal{A}}_i}|\widetilde{i,\alpha}\rangle\langle\widetilde{i+1,\beta}| + \text{H.c.}] \\ &+ \sum_{i=1}^{N} [\epsilon_\alpha|i,\alpha\rangle\langle i,\alpha| + \epsilon_\alpha|\widetilde{i,\alpha}\rangle\langle\widetilde{i,\alpha}|],\end{aligned} \tag{1}$$

where the kets $|i,\alpha\rangle$ and $|\widetilde{i,\alpha}\rangle$ represent the localized basis of the base i on one strand and on its complementary strand, respectively, with α and β denoting the base species, namely, $\alpha,\beta\in\{G,C,A,T\}$. The tight-binding parameters $t_\perp$, $t_\parallel$, and ϵ measure the interstrand hopping, intrastrand hopping, and the on-site energy, respectively. The parameter values adopted for our computation are presented in Table I. In consideration of the molecular geometry, the DNA of helical structure is regarded as a twisted ladder. For its circular (linear) form, periodic (open) boundary conditions are imposed. The presence of a magnetic field of strength B has been taken care of by introducing phase factors in the intrastrand hopping integral, $e^{\pm i\mathcal{A}_i}$ on the one strand and $e^{\pm i\tilde{\mathcal{A}}_i}$ on the other in such a way that $\mathcal{A}_i+\tilde{\mathcal{A}}_i=4\pi f/N$ and $\mathcal{A}_i-\tilde{\mathcal{A}}_i=2\pi\phi_i$ [11]. Here two characteristic fluxes (measured in units of the flux quantum Φ_0 hereafter) are introduced: $f=BS_R/\Phi_0$ representing the flux through the helical axis ring. For defining f as a flux scale common for the closed and the open ring, we take $S_R=(Na)^2/(4\pi)$ with a being the interbase distance ($a=3.4$ Å). The flux through the ith plaquette of the twisted ladder is denoted to be $\phi_i=Bs_i/\Phi_0$, where s_i is its area projected onto the direction of the applied magnetic flux. Due to the twisted structure, the plaquette area s_i varies along the duplex, and reads $s_i=(S_L/2)[\cos i\theta_w+\cos(i+1)\theta_w]\equiv\gamma S_R\mathcal{T}_i$, where θ_w is the twist angle of the base and $S_L=ab$ with the helix diameter $b=10$ Å is the plaquette area for $\theta_w=0$, scaled by the area ratio $\gamma=S_L/S_R$. For circular DNA, N-twist by the angle θ_w must be an integer multiple of 2π, and we thus have $N\theta_w=2\pi L_k$ with the linking number L_k. Accordingly, the phase factors for the twisted structure are given by $\mathcal{A}_i=2\pi f/N+\pi\gamma f\mathcal{T}_i$ and $\tilde{\mathcal{A}}_i=2\pi f/N-\pi\gamma f\mathcal{T}_i$. Plugging these into the Hamiltonian in Eq. (1), we obtain the magnetization at zero temperature via $M=-\partial E_{gs}/\partial B$, where E_{gs} is the ground-state energy.

In the general case, complications arise from the heterogeneity of the sequence and nonuniformity of the flux distribution over the space; the simplest system without such complications would be the untwisted DNA molecules with homogeneous sequence, such as poly(dG)-poly(dC) and poly(dA)-poly(dT) molecules with $\theta_w=0$. As a simple example, we thus consider the poly(dA)-poly(dT) molecule, for which we have $t_\perp^{(\alpha\beta)}=t_\perp^{(AT)}\equiv t_\perp$, $\epsilon_\alpha=\epsilon_A$, and $t_\parallel^{(\alpha\beta)}=t_\parallel^{(AA)}\equiv t_A$ for the adenine chain, and similarly for the thymine chain. Since $\mathcal{T}_i=1$ for $\theta_w=0$, the phase factors in the untwisted geometry are constants independent of the position index [see Eq. (2)]. As a result, the Hamiltonian can be readily diagonalized as

$$\mathcal{H} = \sum_k [E_+(k)h_k^\dagger h_k + E_-(k)\ell_k^\dagger\ell_k] \tag{2}$$

with $(\ell_k,h_k)=(A_k,T_k)U(\phi)$, where $U(\phi)$ is the SU(2) rotation operator with angle defined by $\tan 2\phi=2t_\perp/(E_T-E_A)$ and A_k/T_k is the Fourier transformed basis of the kets on the adenine/thymine strand. The energy levels are given by $E_\pm=(1/2)[E_A+E_T\pm\sqrt{(E_A-E_T)^2+4t_\perp^2}]$, where the dispersions for the decoupled strands ($t_\perp=0$) have been defined to be $E_A=\epsilon_A-2t_\parallel^{(A)}\cos(k_A)$ for the adenine strand and similarly $E_T(k)$ for the thymine strand. Note here that they have different kinematic momenta due to the different phase shifts, $k_A\equiv k+2\pi f/N+\pi\gamma f$ and $k_T\equiv k+2\pi f/N-\pi\gamma f$, where periodic boundary conditions imposed on k lead to $k=2\pi n/N$ with n being integers. Noting that the interstrand hopping is in general much weaker than the intrastrand hopping, known from the first principle studies, we write the energy levels in the approximate form: $E_+(k)\approx E_T(k_T)+t_\perp^2/(E_T-E_A)$ and $E_-(k)\approx E_A(k_A)-t_\perp^2/(E_T-E_A)$. The upper band E_+ and the lower band E_- correspond to the LUMO and the HOMO, respectively, and the gap between them is responsible for the semiconducting nature of the homopolymer [1,14].

To compute the magnetization at half-filling, we sum the energy levels of the HOMO band and obtain, for small flux ($\gamma f\ll 1$), $E_{gs}\approx-\pi^2NT\Delta^{-3/2}(t_\perp\gamma f)^2$, with $\Delta\equiv(\epsilon_T-\epsilon_A)^2-4(t_\parallel^{(T)}-t_\parallel^{(A)})^2$ and $T\equiv 8t_\parallel^{(T)}t_\parallel^{(A)}$. This in turn gives the magnetization per base pair:

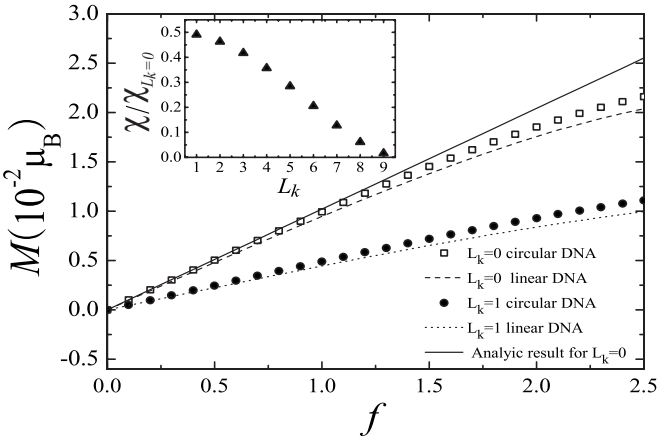

FIG. 2. Magnetization of the poly(dA)-poly(dT) molecule with $N=20$, which does not differentiate the ring geometry from the linear one. The inset shows the linking-number dependence of the orbital susceptibility $\chi=\partial M/\partial B$.

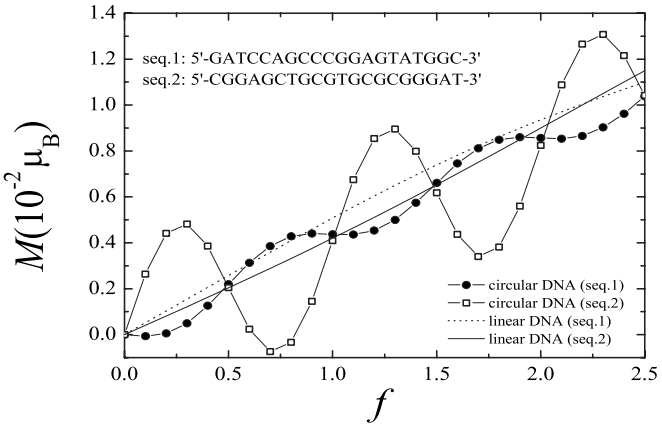

FIG. 3. Magnetization of randomly sequenced DNA. DNA in the circular form exhibits sequence-specific oscillations in the magnetization around that of linear DNA. For DNA of sequence 2, the oscillation amplitude is large so that there exists a flux range for diamagnetism.

$$\frac{M}{N} \approx -\frac{S_R}{N\Phi_0}\frac{\partial E_{gs}}{\partial f} \approx \frac{2\pi^2 t_\perp^2 TS_L}{\Delta^{3/2}}\frac{BS_L}{\Phi_0^3}, \tag{3}$$

which discloses that the magnetization depends on the interstrand hopping integral as $M \propto t_\perp^2$. This suggests that when the ring closure of the DNA helix is considered as two decoupled rings, no magnetization should be appreciable. This may be understood as follows: For $t_\perp=0$, the energy levels of the thymine strand (LUMO) are completely unoccupied [15], so as to yield null contribution to the ground-state energy. On the other hand, those of the adenine strand (HOMO) are fully occupied, which again makes a trivial contribution to the magnetization. To see this more clearly, we assume that the adenine strand accommodates N_e particles, and obtain $E_{gs} \propto \sin(\pi N_e/N)\cos[(2\pi/N)(1/2+f)]$, which is flux independent for $N_e=N$. Note also that in Eq. (3) the effective flux governing the ground-state properties is given by BS_L/Φ_0, i.e., the flux through the helical face. In remarkable consequence, the magnetization of DNA in the circular structure should be the same as that of linear DNA.

For confirmation, we compute numerically the magnetization with the appropriate twist taken into account and present the results in Fig. 2. It is observed that consistently with the above analytical results (albeit limited to the untwisted case), the magnetization of circular DNA (data points) is indeed the same as that of linear DNA (broken lines). In particular, the magnetization for $\theta_w=0$ (or $L_k=0$) shows good agreement with the analytical results for the untwisted geometry (plotted with the solid line). Another key feature here is the paramagnetic behavior of linear DNA, irrespectively of sequence heterogeneity (see also Fig. 3 for randomly sequenced DNA). This is well consistent with the experiment reporting paramagnetism at low temperatures [4]. In addition, we find that the magnetic susceptibility depends on the linking number (see the inset of Fig. 2). This becomes clear by noting the twist-angle dependence of the projected area: A more rapid helical turn makes the duplex thinner. Although experimental observation would be complicated by various types of structural deformation and requires a highly sensitive detector, the linking-number dependence of the orbital susceptibility suggests a possible application to the detection of changes in the helical repeat.

Let us now consider DNA with sequence randomness which prohibits the particles from populating exclusively one of the strands. It is thus readily expected that the ring geometry comes into play and the magnetization should exhibit characteristic oscillations with period $f=1$ [7]. This is indeed the case, as shown in Fig. 3. While linear DNA shows monotonic growth in paramagnetism with increasing the applied flux, the magnetization of circular DNA oscillates around that of linear DNA, and manifests a sequence-specific pattern. Systematic studies of the sequence dependence of DNA magnetization are yet to be done and are expected to provide potential usage to identify DNA sequences. We would mention here that the sign of oscillating components is random, depending on the disorder configuration [7,8]. Therefore, in an experiment on a collection of rings, the oscillating behavior might not be observed in the average magnetization $\langle M\rangle$; instead it is appropriate to measure the typical magnetization $M_{\mathrm{typ}} \equiv \sqrt{\langle M^2\rangle}$. We compute M_{typ} with the average taken over 100 sequences for given base content and present the results in Fig. 4, which provides two suggestions for experimental observation of the oscillating magnetization: Desired are higher contents of guanine and cytosine, which is known to have larger π-orbital overlap. In addition, note that disorder from the sequence randomness puts the molecules in the localized regime where M_{typ} reduces exponentially with the ring size [8]; this is shown in the inset of Fig. 4 as $\ln M_{\mathrm{typ}} \sim -N$. In this respect, small-size rings would be advantageous. Although to realize the flux $f \sim 1$ through a small area demands strong magnetic fields, the maximum field strength is estimated to be about 100 T [16], making it still challenging.

In summary, we have investigated the orbital magnetization of relaxed circular DNA. For homogeneously sequenced DNA, the circular structure has been shown not discernible from the linear form, as far as the magnetization is concerned. On the other hand, sequence heterogeneity gives rise

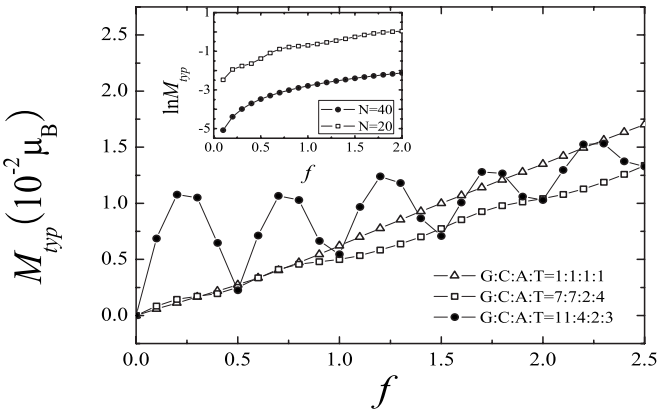

FIG. 4. Typical magnetization of circular DNA. For given base content 10^2 sequences are randomly generated to show that the oscillation amplitude is enlarged by high *GC* contents. The inset shows the exponential dependence of M_{typ} on the ring size *N*.

to sequence-specific oscillations. For an ensemble of DNA rings, we have computed the typical magnetization, the oscillation amplitude of which is shown to depend on the *GC* content as well as on the size of the ring. While the present work is devoted to the zero-temperature behavior, the temperature dependence of the magnetic properties would be a crucial issue. A simple way would be to evaluate the free energy to substitute for the ground-state energy. Here, however, complications at finite temperatures should be properly considered, related with, e.g., phase coherence and thermal noise. Particularly for DNA molecules, temperature effects are associated with the problem of the structural deformation due to their low elastic modulus of the thermal energy scale [17]. It has been shown that when DNA is stretched over its natural length, the hopping parameters are greatly reduced [18]. Finite slides are shown to change the width and the location of the conduction channel [19]. All of these issues and others are of much importance and left for further study.

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[1] P. de Pablo *et al.*, Phys. Rev. Lett. **85**, 4992 (2000); D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, Nature (London) **403**, 635 (2000); A. Kasumov *et al.*, Science **291**, 280 (2001).
[2] E. Shapir *et al.*, J. Phys. Chem. B **109**, 14270 (2005).
[3] F. L. Gervasio, P. Carloni, and M. Parrinello, Phys. Rev. Lett. **89**, 108102 (2002); A. Hübsch, R. G. Endres, D. L. Cox, and R. R. P. Singh, *ibid.* **94**, 178102 (2005).
[4] S. Nakamae, M. Cazayous, A. Sacuto, P. Monod, and H. Bouchiat, Phys. Rev. Lett. **94**, 248102 (2005).
[5] E. B. Starikov, Phys. Rev. Lett. **95**, 189801 (2005); see also S. Nakamae, M. Cazayous, A. Sacuto, P. Monod, and H. Bouchiat, *ibid.* **95**, 189802 (2005).
[6] K. Mizoguchi, S. Tanaka, and H. Sakamoto, Phys. Rev. Lett. **96**, 089801 (2006); see also S. Nakamae, M. Cazayous, A. Sacuto, P. Monod, and H. Bouchiat, *ibid.* **96**, 089802 (2006).
[7] R. Landauer and M. Büttiker, Phys. Rev. Lett. **54**, 2049 (1985).
[8] H.-F. Cheung, E. K. Riedel, and Y. Gefen, Phys. Rev. Lett. **62**, 587 (1989); G. Montambaux, H. Bouchiat, D. Sigeti, and R. Friesner, Phys. Rev. B **42**, 7647 (1990); F. von Oppen and E. K. Riedel, Phys. Rev. Lett. **66**, 84 (1991).
[9] A. Vologodskii, *Topology and Physics of Circular DNA* (CRC Press, Boca Raton, FL, 1992).
[10] J. Yi, Phys. Rev. B **74**, 212406 (2006).
[11] Y. Aharonov and D. Bohm, Phys. Rev. **115**, 485 (1959).
[12] H. Y. Zhang *et al.*, J. Chem. Phys. **117**, 1 (2002).
[13] H. Mehrez and M. P. Anantram, Phys. Rev. B **71**, 115405 (2005).
[14] E. Artacho *et al.*, Mol. Phys. **101**, 1587 (2003); M. S. Xu *et al.*, Appl. Phys. Lett. **87**, 83902 (2005).
[15] The density operators of electrons occupying the lower band and the upper band are respectively given by $\ell^\dagger \ell \approx A^\dagger A + \delta \mathrm{Re}[A^\dagger T]$ and $h^\dagger h \approx T^\dagger T - \delta \mathrm{Re}[T^\dagger A]$ with $\delta \equiv 2t_\perp/(E_T - E_A)$. This indicates that for half-filling, the electron population is localized largely on the adenine strand, apart from the δ-term representing the interstrand orbital mixing linear in $t_\perp$.
[16] J. Sims *et al.*, IEEE Trans. Appl. Supercond. **10**, 510 (2000).
[17] N. Theodorakopoulos, T. Dauxois, and M. Peyrard, Phys. Rev. Lett. **85**, 6 (2000); I. Borukhov, R. F. Bruinsma, W. M. Gelbart, and A. J. Liu, *ibid.* **86**, 2182 (2001).
[18] P. Maragakis, R. L. Barnett, E. Kaxiras, M. Elstner, and T. Frauenheim, Phys. Rev. B **66**, 241104(R) (2002).
[19] Ch. Adessi, S. Walch, and M. P. Anantram, Phys. Rev. B **67**, 081405(R) (2003); Ch. Adessi and M. P. Anantram, Appl. Phys. Lett. **82**, 2353 (2003).