Conversion of twisted light to twisted excitons using carbon nanotubes

Xiaoning Zang1, Nirpendra Singh1,2, Mark T. Lusk3,5 and Udo Schwingenschlögl1,6

Carbon nanotubes are explored as a means of coherently converting the orbital angular momentum of light to an excitonic form that is more amenable to quantum information processing. An analytical analysis, based on dynamical conductivity, is used to show that orbital angular momentum is conserved, modulo $N$, for a carbon nanotube illuminated by radially polarized, twisted light. This result is numerically demonstrated using real-time time-dependent density functional theory which captures the absorption of twisted light and the subsequent transfer of twisted excitons. The results suggest that carbon nanotubes are promising candidates for constructing optoelectronic circuits in which quantum information is more readily processed while manifested in excitonic form.

INTRODUCTION

Centrosymmetric molecules can host twisted excitons carrying orbital angular momentum (OAM)1, and this can be employed to mediate algebraic operations involving twisted light2. A chain of these molecules constitutes a conduit for OAM transfer in the form of twisted exciton wave packets with controllable linear momentum3. The interconversion and manipulation of optical and excitonic manifestations of OAM represents a rich field for quantum information processing4. While optical methodologies are already well-established for encoding and transmitting data as OAM5–11, a distinct advantage of excitons is that they can be readily combined and manipulated for quantum information processing1. A chain of molecules is therefore qualitatively different than simply directing twisted light through optical fibers12. The experimental realization of twisted excitons, however, is challenging, because it requires rigidly connected molecules with low reorganization energy.

Carbon nanotubes (CNTs) offer a means transferring the angular momentum of light to excitonic form, processing it, and then converting it back into an optical form. This is because they are structurally rigid and have the requisite $C_{n}$ symmetry13. The Bloch wave functions, therefore, can be constructed using the rotational operator with the OAM as eigenvalue. The fact that the electrons carry OAM has been confirmed theoretically14 and experimentally15. Ultra-long CNTs have been experimentally fabricated16,17 to lengths of as much as half a meter18. CNTs with carbon purity above 99.98% can be synthesized very efficiently19 and 92% yield has been reported for growth of CNTs with specific chirality20. Combined with tunable band gaps, CNTs are promising candidates for optoelectronic applications as in, for example, solar cells21–27. Recently, CNTs are demonstrated to be high-purity and high-efficiency single-photon sources, which makes CNTs promising candidates for on-chip quantum light sources for quantum information28. Although a lot is known about the optoelectronic properties of CNTs29–33, and their exciton dynamics34–35, the interaction with twisted light is essentially unexplored36.

Here we computationally demonstrate that OAM is conserved when CNTs convert twisted light into twisted excitons. We first establish the optical selection rules by deriving the dynamical conductivity based on the helical and rotational symmetries. Then real-time time-dependent density functional theory (RT-TDDFT) is employed to directly simulate the transfer of OAM from twisted light to twisted excitons37. RT-TDDFT includes the multi-level and multi-electron effects omitted by the tight-binding model. We show that CNTs have effectively the same structure as a molecular chain except that there is a constant helical misorientation between neighboring sites as illustrated in Fig. 1a. CNTs are readily available with a wide range of electronic band structures. They are also rigid and have low reorganization energy so that exciton phonon coupling is minimized, helping to support coherence38. Although the extended states of CNTs make this intuitively reasonable, a reorganization energy of tens of meV has been reported in a recent experiment39. The reorganization energy estimated by the peak width of photoluminescence spectra ranges from tens of meV40 to as low as 1 meV41. This is comparable to the most rigid porphyrins42,43. CNTs therefore offer an ideal setting for the realization of twisted exciton circuitry.

The central concept can be elucidated using a tight-binding model with coupling between the $p_{z}$ orbitals of neighboring carbon atoms. The resulting band structure and eigenstates can then be expressed in terms of crystal momentum due to translational symmetry along the principal axis of the CNT44. However, the required computational time can be dramatically reduced by exploiting helical and rotational symmetries instead45. This approach also is advantageous in that the OAM is related to irreducible representations of SO(2) for continuous space and $C_{n}$ for discrete space. Each eigenstate can be identified with a helical quantum number, $\kappa$, for the twist of subsequent structural units along the axis and a rotational quantum number, $q$, due to the rotational symmetry of structural strands of which the tube is composed. Phonon effects are disregarded under the reasonable assumption that reorganization energy is so low for the extended states of this system exciton wave packet coherence is maintained during the information processing. This can be elucidated by considering a dimer consisting of the first two sites in Fig. 1a38,46, for which the decoherence rate $\Gamma$ can be analytically calculated as

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which is estimated to be in the order of 10 ps \(41\), are much larger than 21 fs. This result is based on the estimate that the coupling between nearest-neighbor arms of the same color. Figures 1 and 2 show that the exciton transfer time in a 4 nm (3,3) CNT (see Fig. 7). Then the sum of a pure dephasing rate \(R_d\) and a relaxation rate \(R_r\):

\[
R = R_d + R_r
\]

\[
R_d = \delta \varepsilon^2 S(0)/(2b^2)
\]

\[
R_r \approx 4J^2 S(b)/(2b^2).
\]

Here \(S(b) = \delta \varepsilon^2 + 4J^2\) with \(\delta \varepsilon\) and \(J\) being the onsite energy difference and the coupling between these two sites, respectively. The thermally weighted spectral density is

\[
S(\omega) = 2\pi \coth[\hbar\omega/(2k_BT)] \sum_i \omega_i d_i^2 \delta(\omega - \omega_i)
\]

with \(d_i\), \(\omega_i\), and \(K_p\) being the strength of electron-phonon coupling, the frequency of the phonon mode, and Boltzmann’s constant, respectively. The reorganization energy is

\[
\lambda = \sum \hbar\omega_i d_i^2 \approx \sum \lambda_i(\omega_i).
\]

Since all sites in a given CNT have the same onsite energy, we have \(R_d = 0\) and \(D = 2J^2 = 2|V_{ph}|\) where \(V_{ph} = 2.77\) eV \(47\) is the coupling between nearest \(p_z\) orbitals in CNTs. Thus \(R = \hbar \lambda(\omega)/2\) is much less than \(\hbar\lambda/2\) and the coherence time \(1/R\) is much larger than 21 fs. This result is based on the estimate that \(\lambda = 10\) meV. Both the coherence time and the exciton life time, which is estimated to be in the order of 10 ps \(41\), are much larger than the exciton transfer time in a 4 nm (3,3) CNT (see Fig. 7). Then a momentum conservation is associated with the photo-excitation of an electron from a valence state with quantum numbers \(\kappa\) and \(q\) to a conduction state with quantum numbers \(\kappa'\) and \(q'\). Specifically, \(q' = q\) and \(\kappa' = \kappa\) must be equal to the photonic angular momentum (PAM) and helical momentum of the twisted light, respectively.

The OAM conservation between excitons and photons can be studied within the context of band structure. The OAM of the exciton (XAM) is the total OAM of all occupied Bloch states and is also the sum of the OAM of all electrons in conduction bands (EAM) and all holes in valence bands (HAM). The fact that the ground state has zero OAM indicates that the EAM associated with an excited electron is the negative of the total EAM from all other electrons. This means that the electron and hole in the same Bloch state are of opposite OAM. It is shown that OAM is conserved during an optical excitation, i.e., PAM = XAM = EAM + HAM. In the absence of meaningful phonon effects, a twisted exciton wave packet transfers down the CNT with the same OAM as was absorbed from twisted light.

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**RESULTS**

**Tight-binding analysis**

A CNT can be created by rolling up graphene along a lattice vector \(\vec{R} = n_1 \vec{e}_1 + n_2 \vec{e}_2\) with the resulting structure characterized by the pair of integers \(n_1, n_2\). Here \(\vec{e}_1\) and \(\vec{e}_2\) are the primitive lattice vectors (Fig. 2). A band gap is present provided \(n_1 - n_2 = 3l \pm 1, \quad l \in \mathbb{Z}\)
Examination of the resulting helical and rotational symmetries reveals that each CNT can be viewed as an $M$-site system, with $N$ arms at each site, in which each arm consists of two inequivalent carbon atoms denoted as $A$ and $B$. For the (5,10) CNT of Fig. 2, for instance, there are five arms at each site which are created by rotational operations of the first arm, and these five arms give rise to the entire CNT by $M−1$ subsequent helical operations. Figure 3 shows the spiral formed by following one arm along the different sites. The primitive lattice vector along the helical direction is given by $\vec{H} = \vec{p}_{1} + \vec{p}_{2}, \vec{p}_{2}$ with $p_{1} ≤ p_{2}$ being the smallest nonnegative integers fulfilling $p_{1} + 2p_{2} = N$.

Since our goal is not to generate quantitatively precise band structures, a $n$-band approximation is applied to demonstrate the key idea that CNTs can serve as conduits for OAM transport and thus as building blocks for optoelectronic circuits. The symmetry group generated by the helical operation is isomorphic to the one-dimensional translation group, so that Bloch’s theorem can be readily generalized. Moreover, because the helical and rotational operators commute, we obtain the following symmetry-adapted, generalized Bloch sums:

$$\Phi_{\alpha, n} = \frac{1}{\sqrt{MN}} \sum_{m=1}^{M} \sum_{n=1}^{N} \epsilon_{m}^{(m-1)\kappa} \epsilon_{n}^{(n-1)\kappa} \phi_{\alpha, m, n},$$

where $\epsilon_{m} = e^{i2\pi m/M}$ and $\epsilon_{n} = e^{i2\pi n/N}$. Each Bloch sum is given by three parameters: $\alpha$, $\kappa$, and $q$. While $\alpha$ is $A$ or $B$ (inequivalent carbon atoms), $\kappa$ and $q$ are the quantum numbers associated with the helical and rotational operations, respectively, taking on integer values within the domains $(-\infty, \infty)$ and $(-\frac{N}{2}, \frac{N}{2})$, $M$ is the site number after $M−1$ helical operations and $N$ is the arm number after $N−1$ rotational operations. Moreover, $\phi_{\alpha, m, n}$ is the orbital of the $\alpha$-type carbon atom in arm $n$ at site $m$.

The matrix elements between Bloch sums with different $\kappa$ and $q$ are zero. Thus, the wave functions are linear combinations of basis states,

$$\Psi_{\alpha, q} = c_{\alpha, q}^{A} \Phi_{\alpha, q}^{A} + c_{\alpha, q}^{B} \Phi_{\alpha, q}^{B},$$

with constants $c_{\alpha, q}^{A}$ and $c_{\alpha, q}^{B}$. Inserting this into the Schrödinger equation gives a $2 \times 2$ eigenvalue problem with energies, $\epsilon_{i} |H_{AB}|$, that are functions of the quantum numbers $\kappa$ and $q$:

$$H_{AB} = \sum_{\kappa = 1}^{M} \sum_{q = 1}^{N} \epsilon_{\kappa}^{(\kappa-1)} \epsilon_{q}^{(q-1)} |\Phi_{\alpha, q}^{A}\rangle \langle \Phi_{\beta, q}^{A}|,$$

$$= V_{pnm} \sum_{i,j} \epsilon_{m}^{(i-1)} \epsilon_{n}^{(j-1)} |\epsilon_{i,j}|.$$

Here $V_{pnm}$ is the coupling strength between nearest neighbors (with a value of $-2.77 \epsilon V^{-1}$). $(i,j)$ denotes the nearest neighbors of atom $A$ in arm 1 at site 1, and $H_{0}$ is the one-electron Hamiltonian of the CNT. This allows the band structure (which is a function of $\kappa$ and $q$) to be immediately constructed.

The eigenstates of $H_{0}$ are the Bloch wave functions $|s, q, \kappa\rangle$, $\hat{H}_{0} |s, q, \kappa\rangle = \epsilon_{s,q,\kappa} |s, q, \kappa\rangle$, where $s = \pm$ refers to conduction/valence states.

Turning to the interaction of CNTs with twisted light, an ideal Bessel mode can be written as

$$E(\rho, \phi, z, t) = J_{l}(k_{0} \rho) e^{i\phi} e^{i\omega n t},$$

with $l$ being the $l$-th order Bessel function of the first kind, $(\rho, \phi, z)$ the polar coordinates, $k_{0}$ and $k_{s}$ the wave numbers, and $\omega$ the frequency. For cylindrically polarized twisted light with polarization singularity on the main axis of the CNT, the rotational center of the SO(2) symmetry (twisted light) coincides with that of the CNT symmetry (CNT). Thus, the combined system (twisted light and CNT) and, particularly, the Hamiltonian of the light-matter interaction possess rotational symmetry, i.e., the OAM may be conserved. We adopt radially polarized twisted light, i.e.,

$$\overrightarrow{E} = \vec{e}_{\rho} E_{0} \sin(\phi + k_{s} z - \omega t),$$

with $\vec{e}_{\rho}$ being the radial unit vector and $E_{0}$ the magnitude of the electric field on the surface of the CNT.

Note that $e^{i\phi}$ with $\phi \in [0, 2\pi]$ are the irreducible representations of the rotation group of continuous two-dimensional space, SO(2), where $l$ can be any integer. When twisted light is applied to a CNT, the rotation group becomes $C_{N}$ with the defining representation $e^{i2\pi n/N}$. Since the group is abelian, each element $(n = 1, \ldots, M)$ forms an equivalence class and the number of equivalence classes equals the number of irreducible representations (which must be orthogonal to each other). The dimensions $d_{l}$ of the irreducible representations must satisfy $\sum_{l=1}^{M} d_{l}^{2} = N$, implying $d_{l} = 1$. The identity and defining representation are irreducible representations. As $\sum_{l=1}^{M} e^{i(l-\frac{1}{2})2\pi n} = \delta_{q,0}$, the irreducible representations have the form $e^{i(l-\frac{1}{2})2\pi n} q$, with $q$ being a parameter. The character orthogonality requires $\sum_{q=0}^{N-1} e^{i(l-\frac{1}{2})2\pi n} = \delta_{q,0}$, which is equivalent to choosing $q$ as integers in the interval $(-\frac{N}{2}, \frac{N}{2})$. Therefore, $C_{N}$ has the irreducible representations $e^{i(l-\frac{1}{2})2\pi n}$, $n = 1, \ldots, N$ and $q$ is an integer in the interval $(-\frac{N}{2}, \frac{N}{2})$. Thus, $l$ is reduced to $q$ modulo $N$. For example, $l = 1$ and $-2$ are equivalent in the case of $C_{3}$ symmetry, as both are reduced to $q = 1$, see Fig. 1b-f. This implies

$$\overrightarrow{E} = \vec{e}_{\rho} E_{0} \sin \left(\frac{q(n-1)2\pi}{N} + \frac{k_{s}(m-1)2\pi}{M} - \omega t\right),$$

where $k_{s} = Ml\theta/2\pi$ with $\theta = 2\pi R / |H|$, $R$ is the wave length of the twisted light is assumed to be much larger than the size of the CNT. The helical momentum $k_{\theta}$ is nonzero, as the phase of the twisted light is zero along the $z$-direction, see Fig. 3.
where $\Omega(t)$ is the step function and
\begin{align}
\alpha_{ij}(t) & \equiv -\frac{1}{\hbar} \text{Tr} \left\{ \hat{D}_i(t), \hat{\rho}_0 \hat{\sigma}_j(t) \right\} \\
& = \frac{1}{\hbar} \text{Tr} \left\{ \hat{A}_0 \hat{\sigma}_j(t), \hat{\rho}_0(t) \right\}.
\end{align}
Taking the Fourier transform of Eq. (15), we obtain
\begin{align}
\tilde{j}_i(\omega) &= -\tilde{\alpha}_{i,1}(\omega) \tilde{E}_{\text{un}}(\omega) + \tilde{\alpha}_{i,2}(\omega) \tilde{E}_{\text{cos}}(\omega),
\end{align}
with
\begin{align}
\tilde{\alpha}_{i,j}(\omega) &= \frac{n_{\eta} M}{\hbar^2} \text{Tr} \left\{ \hat{\rho}_0 \hat{J}_j(0), \hat{J}_i(0) \right\} e^{i(\omega - \eta) t} dt \\
\tilde{E}_{\text{un}}(\omega) &= \int_{-\infty}^{\infty} \hat{E}_0 \sin(\omega t) e^{i(\omega - \eta) t} dt \\
\tilde{E}_{\text{cos}}(\omega) &= \int_{-\infty}^{\infty} \hat{E}_0 \cos(\omega t) e^{i(\omega - \eta) t} dt,
\end{align}
where $\eta$ is the phenomenological rate of relaxation and we have used $\hat{J}_i(0) = \frac{1}{M} \hbar^2 \frac{\partial \hat{\rho}_0}{\partial \omega}$. The expression for $\tilde{\alpha}_{i,j}(\omega)$ is the Kubo formula for the dynamical conductivity. Optical selection rules can be established by transformation to the basis $\{s, q, k\}$. The position operator is written as\textsuperscript{52,53}
\begin{align}
\hat{r} &= r_0 \cos \psi \hat{e}_x + r_0 \sin \psi \hat{e}_y + \left( \sin \beta \frac{\partial}{\partial \psi} + \sin \Omega \frac{\partial}{\partial \theta} \right) \hat{e}_z,
\end{align}
where $\beta$ is the angle between the rotational and helical directions, and
\begin{align}
\hat{\Omega} &= \sum_{s, q, k} \int \hat{u}_{q,s,k}(\hat{r}) \frac{\partial \hat{u}_{q,s,k}(\hat{r})}{\partial k} d\hat{r} |s, q, k\rangle |s, q, k\rangle
\end{align}
with $u_{q,s,k}(\hat{r})$ being the Bloch function. We have
\begin{align}
\hat{\rho}_0 &= 2 \int \hat{\rho}_0 (\epsilon_{s,q,k}) |s, q, k\rangle \langle s, q, k| \
\end{align}
with $n_{\eta}$ being the Fermi distribution. Substitution of Eqs. (21)–(23) into Eq. (20) yields the nonzero dynamical conductivity
\begin{align}
\hat{\alpha}_{1,1}(\omega) &= \alpha_{1,2}(\omega) \\
& = \frac{|e| e^2}{2 n_{\eta} m^2 \hbar^2} \sum_{s, q, k} \left( n_{\eta}(\epsilon_{q,s,k}) - n_{\eta}(\epsilon_{q,s+k,k}) \right) \\
& \times |\langle s, q, k| \hat{H}_0 |r_0 \rangle | e^{i0} |s, q, k - k_0\rangle|^2 \\
& \times \left[ -\epsilon_{q,s+k,k} - \epsilon_{q,s,k} + \hbar \omega + i\hbar \eta \right],
\end{align}
where we have used Eq. (16) and the rotating wave approximation. Therefore, $\tilde{j}_i(\omega) = -\tilde{\alpha}_{1,1}(\omega) \tilde{E}_{\text{un}}(\omega)$ and $\tilde{j}_2(\omega) = \tilde{\alpha}_{2,2}(\omega) \tilde{E}_{\text{cos}}(\omega)$. Equation (24) implies that transitions are allowed between bands.
with the OAM difference equal to the PAM, since in the numerator the OAM difference between the two states (\(q\)) is the OAM of the twisted light. In other words, the OAM is conserved modulo \(N\). We show in Fig. 5a the band structure of the (5, 10) CNT with the OAM of the bands indicated. The transitions of an electron from the state \((-2, 0)\) to different conduction states are illustrated in Fig. 5b, showing that \(k_0\) depends on the PAM.

Former studies of the optical selection rules by \(k \cdot p\) theory\(^54\) or, equivalently, by linear expansion of the Hamiltonian at the Dirac points of graphene\(^52\) did not consider the change of the symmetry group from SO(2) to \(C_\infty\) with the consequence that the OAM of both the twisted light and electron could take any integer value for all CNTs. This leads to wrong conclusions. For example, in the case of \(C_3\) symmetry, electrons transfer from the valence band with \(q = 1\) under illumination with \(l = 2\) twisted light to the conduction band with \(q = 3\) according to \(k \cdot p\) theory, while they transfer to the conduction band with \(q = 0\) according to Eq. (24).

Equation (5) has exactly the same form as the tight-binding model for an \(N\)-site chain of \(N\)-arm cofacial molecules\(^4\). Therefore, \(\sum_{\nu=1}^{N} \varepsilon_{\nu}^{(n-1)q} \mid \phi_{m}^{n} \rangle\) can be considered as a twisted electronic state with OAM \(q\) at site \(m\). The two carbon atoms in one arm have the same phase terms, \(\varepsilon_{\nu}^{(n-1)q}\) and \(\varepsilon_{\nu}^{(n-1)q}\), so that each CNT can be considered as a spiral of \(N\)-arm sites. In order for the exciton to carry nonzero OAM, we require \(N \geq 3\), with \(N\) being the greatest common divisor of \(n_1\) and \(n_2\). This condition must be fulfilled in addition to the requirement that the CNT is semiconducting, see Eq. (4). From Eq. (7), one can expect that each band is associated with a specific OAM. This is demonstrated in Fig. 5, where the band structure of the (5, 10) CNT is plotted with different colors encoding the OAM. The electrons and holes fulfill \(EAM = -HAM\) for a specific band.

OAM conservation between the photon of twisted light absorbed by the CNT and the twisted exciton (\(XAM = EAM + HAM\)) is confirmed by our analysis. For example, when an electron in the valence band with OAM \(-1\) absorbs twisted light with \(PAM = +2\) it is excited into a conduction band with OAM \(+1\). Thus we have an electron with \(EAM = +1\) and a hole with \(HAM = +1\), such that the exciton carries \(XAM = EAM + HAM = PAM\). In general, a twisted exciton with \(XAM = q + nN\) \((q \in [-\frac{n_1}{2}, \frac{n_2}{2}], n \in \mathbb{Z})\) for arbitrary \(n \in \mathbb{Z}\) is equivalent to the twisted exciton with \(XAM = q\). This is analogous to the lack of uniqueness in the definition of crystal momentum, i.e., \(hk = h(k + 2\pi a)\) where \(a\) is the lattice spacing. As a consequence, a twisted exciton with \(XAM = q\) can be generated by twisted light with \(PAM = q + nN\). When \(N\) is even, excited states induced by twisted light with \(|q + nN| = N/2\) have no specific circularity and therefore are not considered\(^55\).

It is worth emphasizing the difference between the important role of the PAM here in contrast to the typically neglected role of the photonic linear momentum in standard band structure theory. In the latter case the linear momentum of the electrons in the valence band is so large that their change in momentum due to photon absorption can be safely ignored at room temperature. Within the CNT setting, though, the PAM is on the same order of magnitude as the EAM of the valence band electrons and the OAM conservation is nontrivial.

**RT-TDDFT analysis**

RT-TDDFT considers multi-level and multi-electron effects omitted in the tight-binding paradigm\(^56\). And it is a computationally cheaper way to study excitonic effects comparing with the Bethe-Salpeter equation. The evolution of the electronic states during the interaction with twisted light can be explicitly tracked within a Kohn–Sham (KS) formulation of the electronic structure, see the Methods section for details. Exciton transport with conserved OAM is demonstrated for a 4 nm long (3, 3) CNT, see Fig. 6a, with hydrogenated ends, because a (5, 10) CNT with sufficient length exceeds the available computational resources. Note that the length of 4 nm is much larger than the diameter (exciton size). The fact that the (3, 3) CNT is metallic does not prohibit demonstration of the core idea since it still has rotational and...
The physics would not change when it was applied to more sites simultaneously, but this would require a longer CNT to observe the exciton wave packet. With phonon coupling disregarded, the laser pulse results in a coherent superposition of the ground and excited states. The electron and hole populations at each site are calculated through integration of the attachment and detachment densities, over a cylinder with the site in the center and with the length being the projection of $H$ on the axis of the CNT. The exciton population is defined as the average of the electron and hole populations. Figure 7 demonstrates that the electrons, holes, and excitons propagate along the CNT. Due to reflection at the other end, finally an equal distribution is established.

To verify the OAM conservation, we first calculate the exciton populations when the system is initially in the ground state. The idea is that small excitations with different OAMs do not influence each other. Note that the long laser pulse in Fig. 6c is employed in the following. Let us denote the excited states with the same OAM (modulo $N$) by $|\Psi(OAM)\rangle$ and the corresponding populations by $p$ (OAM). If there is OAM conservation, then the excited state is $|\Psi(q)\rangle$ and its population is $p(q)$ for twisted light with PAM = $q$. The total exciton population is $\sum p(q)$ when light pulses with different $q$ are applied. This is consistent with the observation $p_0 - p_1 + p_3$ and $p_0 - p_1 + p_2 + p_3$ in Fig. 8. When two pulses of the same twisted light are applied we have 4 times larger population, which is consistent with the observation $p_0 - 4p_1$ in Fig. 8. However, we yet cannot conclude that there is OAM conservation. If $p_1$ in Fig. 8 corresponds to an excited state $a|\Psi(1)\rangle + b|\Psi(-1)\rangle$, then $p_3$ must correspond to the excited state $b|\Psi(1)\rangle + a|\Psi(-1)\rangle$ and we have $p_1 = p_3 = a^2 + b^2$. Thus, the excited state induced by the two twisted light pulses is $(a + b)|\Psi(1)\rangle + (a - b)|\Psi(-1)\rangle$ and its population is $p_3 = 2(a + b)^2$. Assuming $a, b \in \mathbb{R}$, we find $a^2 \sim 2400b^2$ at $t = 25$ fs, which means that twisted light with a specific PAM induces an exciton with pure OAM.

Fig. 6 The (3, 3) CNT. a Decomposition of the (3, 3) CNT into a spiral of 3-arm sites. b Energies of the KS orbitals. The 402nd is the highest occupied KS orbital. Orbitals with OAM = 0 and ±1 are shown in black and cyan, respectively. c Laser pulses with $E_0 = 0.5 \text{ V/Å}$, $\hbar \omega = 2 \text{ eV}$ and envelope function $\exp(- (t - 0.3fs)^2 / 2(0.03fs)^2)$ (red) or $\exp(- (t - 10fs)^2 / 2(3fs)^2)$ (green). The gray curve is $0.5 \sin(\omega t)$. d Normalized Fourier transforms of the curves in c.
Second, we calculate the exciton populations when the system is initially in an excited state with OAM = 1 and population 0.05 ($p_7$ and $p_8$ in Fig. 8). Specifically, one electron is initially excited from a linear combination of the 389th and 390th KS orbitals to the 403rd KS orbital. Since we know that twisted light with PAM = ±1 induces an exciton with pure OAM = ±1, we will have either $p_7 = 0.05 + p_1$ or $p_8 = 0.05 + p_3$. Figure 9 shows $p_7 \approx 0.05 + p_1$, which means that the initial excited state has opposite OAM as compared to the excited state with $p_1$. In other words, the twisted light with PAM = −1 induces an exciton with the same OAM, i.e., the OAM is conserved. Note that the initial excited state has an energy of 2.3 eV, which is not resonant with the frequency of the laser pulse. Thus, it contributes little to the excited state induced by the laser pulse and $p_8$ is similar to 0.05 + $p_3$.

Due to the OAM conservation, the population for each XAM can be determined, see the Methods section for details. Figure 10a shows XAM for twisted light with PAM = −1, 0, and 1. We can conclude that twisted light with PAM = 0 leads to XAM = 0 and twisted light with PAM = ±1 leads to opposite XAMs. Using PAM = −1 as an example, we have XAM = −$p(-1) + 2p(2)$. Together with the normalization condition $p(-1) + p(2) = 1$ this leads to the exciton populations shown in Fig. 10b. The population $p(2)$ is due to excitations from occupied to unoccupied orbitals with OAM = ±1, which have energies of at least 3 eV, see Fig. 6b, i.e., far from resonance with the frequency of the laser pulse. Therefore, $p(2)$ can be neglected and the OAM can be determined in this case.

We next demonstrate conservation of the spin of circularly polarized light, which can be decomposed into radially and azimuthally polarized twisted lights \(^1,6^2\),

\[
\frac{1}{\sqrt{2}} \left( \vec{e}_x \pm i \vec{e}_y \right)
= \frac{1}{\sqrt{2}} \left( \cos \phi \vec{e}_r \mp i \sin \phi \vec{e}_\phi \right) \\
= \frac{1}{\sqrt{2}} e^{\pm i\phi} \left( \vec{e}_r \pm i \vec{e}_\phi \right),
\]

where $\vec{e}_x$, $\vec{e}_y$ and $\vec{e}_r$, $\vec{e}_\phi$ are the unit vectors of Cartesian and polar coordinate systems, respectively, and $e^{\pm i\phi}$ represents OAM = ±1. Right-hand circularly polarized light with spin = −1 is applied along the axis of the CNT. According to Fig. 11, $p_{10} \sim 4p_1$ and $p_{11} \sim p_3 + p_9$ confirm the equivalence of right-hand circularly polarized light with spin = −1 and twisted light with PAM = −1 in the sense that they induce an exciton with the same XAM. Thus, the CNT can convert circularly polarized light into twisted light.

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**Fig. 7 Exciton wave packet.** a Electron and hole populations at different sites as functions of time. b Exciton population at different sites at specific times. The results refer to the short laser pulse of Fig. 6c.
DISCUSSION

We have shown that the orbital angular momentum is conserved during the excitation and subsequent transfer of twisted excitons in CNTs. These have extremely low reorganization energy in comparison to molecular chains implying the possibility of strong band transport and long coherence time for twisted exciton wave packets. CNTs therefore hold promise for exploiting the interplay of photonic and excitonic angular momentum for quantum information processing. The present work initially employs tight-binding analysis based on the helical and rotational symmetries to derive the dynamical conductivity. The obtained optical selection rules show OAM conservation and non-vertical transitions between bands for $\text{OAM} \neq 0$. The advantage of using the helical and rotational symmetries is that the $\text{CN}_2$ rotation group of CNTs is considered automatically. Traditional derivations of the optical selection rules, by employing $k \cdot p$ theory or equivalently by linear expansion of the Hamiltonian around the Dirac points of graphene, are actually based on the rotation group $\text{SO}(2)$, which leads to wrong conclusions on the optical excitations of CNTs illuminated by twisted light.

We employ the RT-TDDFT approach, which includes multi-level and multi-electron effects, being computationally cheaper than the Bethe-Salpeter equation, for the study of excitons. The results confirm that the OAM is conserved in the presence of electron-hole interaction, between photon and exciton as well as during exciton transfer. Former studies have shown that OAM cannot be exchanged between twisted light and the electrons of isolated atoms by dipole transition\cite{63-67}. However, this does not apply to a ring of atoms with $\text{CN}_2$ symmetry\cite{1}, as each atom can be excited by dipole transition and pick up the specific phase of the twisted light at its position, giving rise to a collective mode. The reverse process, generation of twisted light via the dipole transition of molecules in a ring, has been demonstrated in ref.\cite{55}.

Fig. 8  Twisted light to twisted exciton. Exciton populations in a 4 nm long (3, 3) CNT illuminated by a twisted light pulse with PAM = $-1$ ($p_1, p_7$), 0 ($p_2$), or 1 ($p_3, p_8$), twisted light pulses with PAM = $-1$ and 1 of the same amplitude ($p_4$), twisted light pulses with PAM = $-1, 0$, and 1 of the same amplitude ($p_5$), and two twisted light pulses with PAM = $-1$ of the same amplitude ($p_6$). The CNT is initially in the ground state for $p_1$ to $p_6$ and in a 0.95:0.05 superposition of the ground state and excited states for $p_7$ and $p_8$.

Fig. 9  Exciton population differences. $p_7 - (0.05 + p_1)$ (green) and $p_8 - (0.05 + p_2)$ (blue), compare Fig. 8. Black dashed lines indicate the average in the respective region.

Fig. 10  OAM conservation. a $\text{XAM}$ obtained for twisted light with PAM = $-1$ (green), 0 (black), and 1 (blue). b Corresponding exciton populations.
METHODS

Time-dependent Kohn–Sham formulation

Denoting the external potential (nuclei and light field) as \( v_{\text{ext}} \) the Hartree potential as \( v_{\text{H}} \) and the exchange-correlation potential as \( v_{\text{xc}} \), we have

\[
\frac{\hbar}{\beta} \frac{\partial}{\partial t} |\psi(r, t)\rangle = -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(r, t) + v_{\text{H}}|\psi(r, t)\rangle \\
+ v_{\text{xc}}[\rho(r, t)] |\psi(r, t)\rangle
\]

where \( \rho(r, t) = \sum_{j=1}^{N} |\psi_j(r, t)\rangle \langle \psi_j(r, t)| \).

Eq. (27) is the spin-reduced density operator of 2N electrons. RT-TDDFT simulations are carried out using the Octopus package with Troullier–Martin pseudopotentials and the Perdew–Burke–Ernzerhof exchange-correlation potential within the generalized gradient approximation. A time step of 0.66 \( \times 10^{-15} \) s is employed together with an atomic sphere radius of 3 Å and a grid size of 0.15 Å.

Average OAM of the exciton

In principle, the total OAM can be calculated as the sum of the OAMs of all states weighted by their populations, which is, however, computationally impossible. The total OAM can also be calculated by summation of the OAMs over all occupied time-propagated KS orbitals. Because of the C\(_2\)v symmetry, the KS orbitals with OAM = 0 are nondegenerate and the KS orbitals with OAM \( \neq 0 \) are twofold degenerate. As we can always construct KS orbitals \( |\psi_j(r, 0)\rangle \) with OAM = \( q \) from \( |\psi_j(r, 0)\rangle \) by the method of ref. 1, the OAM of the \( i \)-th time-propagated KS orbital can be readily calculated as

\[
\text{OAM}_i = \sum_{j=1}^{M} |\langle \psi_j(r, 0)|\psi_i(r, t)\rangle|^2 q_j.
\]

Thus, \( \sum_{i=1}^{M} \text{OAM}_i \) is the total OAM of the time-propagated multi-electron state, which is a linear combination of the ground and excited states. Since the ground state has OAM = 0, the average OAM of the exciton is

\[
\overline{\text{OAM}} = \sum_{i=1}^{M} \text{OAM}_i / \sum_{i=1}^{M} n_i^2
\]

with the total number \( \sum_{i=1}^{M} n_i^2 \) of excitons derived from the positive eigenvalues \( |\langle \rho(r, t) - \rho(0), 0\rangle|^2 q_j \). The overline indicates that this is an average quantity.

Eq. (29) does not recognize the equivalence of OAMs modulo \( N \). For example, in the case of the (3, 3) CNT we have

\[
\overline{\text{OAM}} = \sum_{q=1}^{N} \rho_0^2 (q - q'),
\]

where \( \rho_0^2 \) is the population of the state with one electron excited from the KS orbital with OAM = \( q' \) to that with OAM = \( q \) (the total population of the excited states being normalized to 1). When twisted light with PAM = 1 is applied, we have \( \overline{\text{OAM}} = p_1^2 (1) + p_1^2 (-2) \), which is not equal to the PAM when \( p_1^2 = 0 \). While Eq. (29) thus cannot be used to determine the total OAM of the excitons, it helps to determine the population of each exciton with distinct OAM.

DATA AVAILABILITY

All data generated or analyzed during this study are included in the article.

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REFERENCES

1. Zang, X. & Lusk, M. T. Twisted molecular excitons as mediators for changing the angular momentum of light. Phys. Rev. A 96, 013819 (2017).
2. Allen, L., Beijersbergen, M. W., Spreeuw, R. J. C. & Woerdman, J. P. Orbital angular momentum of light and the transformation of Laguerre-Gaussian laser modes. Phys. Rev. A 45, 8185–8189 (1992).
3. Zang, X., Montangero, S., Carr, L. D. & Lusk, M. T. Engineering and manipulating excitons, it helps to determine the population of each exciton with distinct OAM.

Fig. 11 Circularly polarized light to twisted exciton. Exciton populations in a 4 nm long (3, 3) CNT illuminated by right-hand circularly polarized light (\( \rho_0 \)), right-hand circularly polarized light with spin = −1 and twisted light with PAM = −1 of the same amplitude (\( \rho_0 \)), and right-hand circularly polarized light and twisted light with PAM = 1 of the same amplitude (\( \rho_1 \)). The CNT is initially in the ground state. The \( \rho_1 = \rho_2 \) curve is reproduced from Fig. 8.

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