First-Principles Methodology for Determining the Angular Momentum of Excitons

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Abstract

We develop a methodology for extracting the Kohn-Sham angular momentum of excitons in realistic systems from time-dependent density functional theory. For small systems the exciton populations can be calculated analytically, which allows us to test the methodology for a 3-arm H₂ molecular ring and a pair of such rings. For larger systems the developed methodology opens for the first time a venue to determine the angular momentum of excitons by first principles calculations. A chain of twenty 3-arm H₂ molecular rings and a triphenylphosphine molecule are investigated as illustrative examples. It is demonstrated that the angular momentum is conserved during the absorption of twisted light.

I. INTRODUCTION

As angular momentum (AM) can serve as extra degree of freedom for encoding information¹, research efforts towards utilization of twisted light (light carrying AM) have been made both in classical^{2–4} and quantum communication^{5–15}. A variety of setups for generating twisted light have been developed, such as spatial light modulators^{16,17}, spiral phase plates¹⁸, q plates^{19–22}, homogeneous uniaxial birefringent crystals^{23–27}, molecular arrays^{28,29}, and metasurfaces^{30–32}. Experiments have demonstrated distinguishable modes of twisted light even after a transmission of 143 km³³. In addition, quantum entanglement of states with AM > 10000 has been observed in Ref. 34.

Only recently there are attempts to manipulate the AM of twisted light by excitons^{35,36}. An exciton is a unit vector on a Bloch sphere when considered as quantum bit and can be rotated by applying laser pulses^{37–44} to realize operations of quantum logic gates. There exist devices for storing excitons^{45,46} and controlling excitons by electric fields^{47,48}. In addition, gating architectures⁴⁹, excitonic transistors^{50–52}, exciton conveyors⁵³, and devices for directed exciton transfer^{54,55} have been reported. This technical progress makes it possible to employ excitons to efficiently process and manipulate information encoded in light by bridging the gap between photonics and electronics⁵⁶. An exciton that is generated by illuminating a molecule with C_N ($N \geq 3$) symmetry by twisted light, for example, obtains the AM of the absorbed photon, and it turns out that a chain of such molecules can be used to create excitonic wave packets with well defined linear and angular momenta^{35,36,57}. A succession of absorption events generates excitonic wave packets carrying a range of AM. The fact that the modified AM can be transferred back to a photon by emission implies that excitons are able to mediate a change in the AM of twisted light.

In order to examine excitons in real molecules, such as triphenylphosphine, hexaphenylbenzene, and coronene, we develop in the present work a methodology for extracting the Kohn-Sham (KS) AM from calculations within time-dependent density functional theory (TDDFT). This first-principles methodology is first tested for a 3-arm H_2 molecular ring and a pair of such rings, because the populations of excitons with different AM can be calculated analytically for both these systems. Afterwards, we apply it to a chain of twenty 3-arm H_2 molecular rings as well as to a triphenylphosphine molecule.

II. METHODOLOGY

TDDFT is a computationally cheaper method for treating excitonic effects than solving the Bethe-Salpeter equation and gives more accurate results than the tight-binding model (as multi-level and multi-electron effects are included). The evolution of the electronic states during the interaction with twisted light is given by the KS formulation⁵⁸

$$i\hbar \frac{\partial}{\partial t} |\psi_i(r, t)\rangle = \left[-\frac{\hbar^2}{2m} \nabla^2 + \nu_{ext}(r, t) + \nu_{Ha}[\rho](r, t) + \nu_{xc}[\rho](r, t) \right] |\psi_i(r, t)\rangle \quad (1)$$

$$\rho(r, t) = 2 \sum_{i=1}^M |\psi_i(r, t)\rangle \langle \psi_i(r, t)|, \quad (2)$$

where ν_{ext} , ν_{Ha} , and ν_{xc} are the external potential (nuclei and light field), Hartree potential, and exchange-correlation potential, respectively. Eq. (2) is the spin-reduced density operator of $2M$ electrons. Each time-propagated KS orbital can be expanded in the basis of KS orbitals at $t = 0$,

$$|\psi_i(r, t)\rangle = \sum_{j=1}^L \langle \psi_j(r, 0) | \psi_i(r, t) \rangle |\psi_j(r, 0)\rangle, \quad (3)$$

with L large enough to make the basis approximately complete. Thus, the multi-electron wave function, which is the Slater determinant of the M occupied time-propagated KS orbitals, can be written as a linear combination of Slater determinants constructed from the M occupied and $L - M$ lowest unoccupied KS orbitals at $t = 0$ assuming that all excited states are one-electron excitations⁵⁹,

$$|\Psi(t)\rangle = c_0(t) |\psi_1(r, 0)\psi_2(r, 0) \cdots \psi_M(r, 0)\rangle + \sum_{i=1}^M \sum_{a=1}^{L-M} c_i^a(t) |\Psi_i^a\rangle, \quad (4)$$

where $|\Psi_i^a\rangle = |\psi_1(r, 0) \cdots \psi_i(r, 0) \cdots \psi_M(r, 0)\rangle$ is the Slater determinant with the i -th occupied KS orbital replaced by the a -th unoccupied KS orbital.

Real-time TDDFT can be used to generate real KS wave functions at $t = 0$. Because of the C_N symmetry of the investigated systems, the KS orbitals with $AM = 0$ are nondegenerate and those with $AM \neq 0$ are twofold degenerate. Out of each pair of degenerate KS orbitals $|\psi_i(r, 0)\rangle$, $|\psi_j(r, 0)\rangle$ we can always construct orbitals with opposite AM, specifically $|\phi_i\rangle = (|\psi_i(r, 0)\rangle + i|\psi_j(r, 0)\rangle)/\sqrt{2}$, $|\phi_j\rangle = (|\psi_i(r, 0)\rangle - i|\psi_j(r, 0)\rangle)/\sqrt{2}$. In Fig. 1 we give examples of this construction for a 3-arm H_2 molecular ring and a triphenylphosphine molecule. First, each real KS orbital is decomposed in the basis of arm orbitals. For example, $|\psi_{HOMO-1}\rangle =$

FIG. 1: Arms of (a) a 3-arm H_2 molecular ring and (d) a triphenylphosphine molecule. Corresponding wave functions are shown in (b, c) and (e, f), respectively.

$(|2\rangle - |3\rangle)/\sqrt{2}$, $|\psi_{\text{HOMO}}\rangle = (-\sqrt{4}|1\rangle + |2\rangle + |3\rangle)/\sqrt{6}$ for the 3-arm H_2 molecular ring and $|\psi_{\text{LUMO}+1}\rangle = (|2\rangle - |3\rangle)/\sqrt{2}$, $|\psi_{\text{LUMO}}\rangle = (-\sqrt{4}|1\rangle + |2\rangle + |3\rangle)/\sqrt{6}$ for the triphenylphosphine molecule. For an N -arm system the wave function with $\text{AM} = q_k$ is

$$|\nu_{q_k}\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i2\pi(j-1)q_k/N} |j\rangle. \quad (5)$$

We then construct

$$|\phi_k\rangle = \langle\psi_i(r, 0)|\nu_{q_k}\rangle |\psi_i(r, 0)\rangle + \langle\psi_j(r, 0)|\nu_{q_k}\rangle |\psi_j(r, 0)\rangle \quad (6)$$

assuming that $|\psi_i(r, 0)\rangle$ and $|\psi_j(r, 0)\rangle$ are degenerate. This leads to $|\phi_{\text{HOMO}-1}\rangle = (|\psi_{\text{HOMO}-1}\rangle + i|\psi_{\text{HOMO}}\rangle)/\sqrt{2}$ with $\text{AM} = 1$ and $|\phi_{\text{HOMO}}\rangle = (|\psi_{\text{HOMO}-1}\rangle - i|\psi_{\text{HOMO}}\rangle)/\sqrt{2}$ with $\text{AM} = -1$ for the 3-arm H_2 molecular ring. Similarly, we obtain $|\phi_{\text{LUMO}+1}\rangle = (|\psi_{\text{LUMO}+1}\rangle + i|\psi_{\text{LUMO}}\rangle)/\sqrt{2}$ with $\text{AM} = 1$ and $|\phi_{\text{LUMO}}\rangle = (|\psi_{\text{LUMO}+1}\rangle - i|\psi_{\text{LUMO}}\rangle)/\sqrt{2}$ with $\text{AM} = -1$ for the triphenylphosphine molecule.

Using the new orbitals as basis, the ground state $|\phi_1\phi_2\cdots\phi_M\rangle$ is identical to $|\psi_1(r, 0)\psi_2(r, 0)\cdots\psi_M(r, 0)\rangle$, as we have just performed a basis change. For each excited state $|\Phi_k^b\rangle$ (Slater determinant for exciting one electron from the k -th occupied orbital to the b -th unoccupied orbital) the population can be calculated from Eq. (4) as

$$P_k^b = \left| \sum_{i=1}^M \sum_{a=1}^{L-M} \langle\phi_b|\psi_a(r, 0)\rangle \langle\psi_i(r, 0)|\phi_k\rangle c_i^a(t) \right|^2. \quad (7)$$

As the ground state has $\text{AM} = 0$, the nonzero AM of the excited state $|\Phi_k^b\rangle$ must be caused by the replacement of $|\phi_k\rangle$ by $|\phi_b\rangle$. The AM of $|\Phi_k^b\rangle$ is therefore obtained by subtracting the AM of $|\phi_k\rangle$ from that of $|\phi_b\rangle$.

While analytically we can calculate by Eq. (7) the population of each excited state and thus the average AM of the exciton ($\overline{\text{XAM}}$), the coefficients of $M!$ Slater determinants must be obtained for each single population³⁶. This is computationally not possible for realistic systems with more than a few electrons. Even for a toy system like a chain of 3-arm H_2 molecular rings we are limited to a maximal length of two rings. However the $\overline{\text{XAM}}$ can be readily extracted from the results of a real-time TDDFT calculation, which allows us to study realistic systems. The AM of $|\psi_i(r, t)\rangle$ is given by

$$\text{AM}_i = \sum_{k=1}^L |\langle \phi_k | \psi_i(r, t) \rangle|^2 q_k, \quad (8)$$

where $|\psi_i(r, t)\rangle$ is obtained from the TDDFT calculation and $|\phi_k\rangle$ (with $\text{AM} = q_k$) is calculated by Eqs. (5) and (6). Summation over all time-propagated KS orbitals, $\sum_{i=1}^M \text{AM}_i$, gives the total AM of the time-propagated multi-electron state, which, however, is a linear combination of ground and excited states. Since the ground state has $\text{AM} = 0$ and the total number of excitons, $\sum_{j=1}^{L/2} n_j^2$, depends only on the positive eigenvalues $\{n_j\}$ of the operator $(\rho(r, t) - \rho(r, 0))/2^{60}$, i.e., it is available from the TDDFT calculation, we can readily evaluate the relation

$$\overline{\text{XAM}} = \sum_{i=1}^M \text{AM}_i / \sum_{j=1}^{L/2} n_j^2. \quad (9)$$

III. COMPUTATIONAL RESULTS

All real-time TDDFT calculations are carried out using OCTOPUS⁶¹ with Troullier-Martins pseudopotentials and the generalized gradient approximation of the exchange-correlation functional (as parametrized by Perdew, Burke, and Ernzerhof). Spheres of radius 3 Å are chosen around each atom and are discretized by grids with a spacing of 0.15 Å. The time step is chosen to be 0.001 fs. The Hamiltonian of the light-matter interaction is

$$\hat{H}_{int}(r, t) = -e\vec{r} \cdot \vec{E} e^{-(t-t_0)^2/2\tau^2} e^{i\omega t}, \quad (10)$$

where e is the elementary charge and $\vec{E}$ ($|\vec{E}| = 0.05 \text{ V/\AA}$) is the electric field of a circularly polarized light (which is equivalent to twisted light with $\text{AM} = \pm 1^{62}$). The light has a

FIG. 2: RT-TDDFT applied to a 3-arm H_2 molecular ring illuminated by circularly polarized light with spin 1 (purple) and spin -1 (red): (a) $\overline{\text{XAM}}$ as obtained from Eq. (9). (b) Population of the excited state with $\text{AM} = 1$ (purple) and $\text{AM} = -1$ (red). The structure of the 3-arm H_2 molecular ring (radius $2 \text{ \AA}$; H-H bond length $0.74 \text{ \AA}$) is shown as inset.

Gaussian envelope with $t_0 = 7.25 \text{ fs}$ and $\tau = 1.93 \text{ fs}$. Its energy ($\hbar\omega$) is set to 10.6 eV for the systems based on H_2 molecular rings and 3.56 eV for the triphenylphosphine molecule.

We first test our methodology by tracking the AM dynamics for a 3-arm H_2 molecular ring and a pair of such rings. When a 3-arm H_2 molecular ring (H-H bond oriented along the radial direction) is illuminated by circularly polarized light with spin ± 1 propagating perpendicularly to the ring, the generated exciton carries $\overline{\text{XAM}} = \pm 1$ according to Eq. (9), see Fig. 2(a). Eq. (7) implies that all excited states with nonzero population have $\text{AM} = \pm 1$, which is shown in Fig. 2(b). Fig. 3(a) demonstrates for a pair of 3-arm H_2 molecular rings with a separation of $20 \text{ \AA}$ that the exciton also carries $\overline{\text{XAM}} = \pm 1$ when one ring is illuminated by circularly polarized light with spin ± 1 (possible by two-photon absorption³⁶). The populations calculated by Eq. (7) are shown in Fig. 3(b). Only excited

FIG. 3: RT-TDDFT applied to a pair of 3-arm H_2 molecular rings with 20 Å separation (see inset) when the first ring is illuminated by circularly polarized light with spin 1 (purple) and spin -1 (red): (a) $\overline{XAM}$ as obtained from Eq. (9). (b) Populations of the four excited states with $AM = 1$ (purple) and $AM = -1$ (red). The total population is shown in black color.

FIG. 4: RT-TDDFT applied to a chain of twenty 3-arm H_2 molecular rings with 20 Å separation: $\overline{XAM}$ as obtained from Eq. (9) when the first ring is illuminated by circularly polarized light with spin 1 (purple) and -1 (red).

states with $AM = \pm 1$ have nonzero populations. Summation gives a total population of the exciton (black curve) consistent with the results in Ref. 36.

Having confirmed the reliability of the proposed methodology, we now apply it to a chain of twenty 3-arm H_2 molecular rings. This system shows exciton wave packet transfer³⁶ but is too complex to derive the $\overline{XAM}$ analytically. Applying Eq. (9), Fig. 4 confirms that the exciton wave packet carries $\overline{XAM} = \pm 1$ when the first ring is illuminated by circularly polarized light with spin ± 1 . Going beyond toy models, we next study a triphenylphosphine molecule. When circularly polarized light with spin ± 1 is applied along the C_3 rotational axis, the exciton carries again $\overline{XAM} = \pm 1$, see Fig. 5(a). Light polarized in a particular direction can be considered as a linear combination of circularly polarized light with spin 1 and spin -1 . When it is applied along the rotational axis of the molecule, states with opposite AM are excited with equal populations and we have $\overline{XAM} = 0$, see the black

FIG. 5: RT-TDDFT applied to a triphenylphosphine molecule: (a) $\overline{XAM}$ as obtained from Eq. (9) for illumination by circularly polarized light with spin 1 (purple) and -1 (red) as well as for light polarized perpendicular to the rotational axis of the molecule (black). (b) Fourier transform of the dipole moment.

FIG. 6: RT-TDDFT applied to a 3-arm H_2 molecular ring illuminated by circularly polarized light with spin -1 : (a) $\overline{\text{XAM}}$ calculated by Eq. (9) (purple) compared to analytical results (green). (b) Energy alignment and involved excitations.

curve in Fig. 5(a). The Fourier transform of the dipole moment in Fig. 5(b) shows that the excited states have an energy of 3.56 eV. By linear-response TDDFT (OCTOPUS), we find that twofold degenerate states $|\Psi_{\text{HOMO}}^{\text{LUMO}}\rangle$ and $|\Psi_{\text{HOMO}}^{\text{LUMO}+1}\rangle$ construct the excited states with $\text{AM} = \pm 1$.

Figure 6(a) shows for a 3-arm H_2 molecular ring illuminated by circularly polarized light with spin -1 ($\hbar\omega = 12$ eV) that the $\overline{\text{XAM}}$ calculated by Eq. (9) (purple dots) is not -1 . This is caused by mixing of excited states with $\text{AM} = -1$ and 2: Fig. 6(b) depicts the lowest 6 orbitals, with the lowest 3 fully occupied in the ground state. There are 3 dominating excitations, for which our methodology finds $\text{AM} = -1$ or 2. Comparison to analytical results (green dots), calculated from the populations of the excited states with $\text{AM} = -1$ (P_{-1}) and $\text{AM} = 2$ (P_2) as $\overline{\text{XAM}} = -1P_{-1} + 2P_2$, confirms that the deviation of $\overline{\text{XAM}}$ from a value of -1 is due to the involvement of the excited state with $\text{AM} = 2$. Physically, $\text{AM} = 2$ is equivalent to $\text{AM} = -1$ because of the reduction of the continuous to a C_3 rotational symmetry. Similar phenomena have been reported for Wannier-Mott excitons^{64,65}.

IV. CONCLUSIONS

As main result, we have developed a first-principles methodology for extracting the KS AM of an exciton, based on time-dependent density functional theory. In particular, this methodology makes it possible to explore the potential of employing AM as extra degree of freedom in classical and quantum communication. Evaluating the AM of an exciton

in terms of excited state populations is only possible for small systems. The developed methodology, on the other hand, provides access to realistic systems. The validity of our approach has been confirmed for two toy systems and then applied to a chain of twenty 3-arm H_2 molecular rings, for which we have demonstrated that the AM is conserved during the process of illumination by twisted light. For a triphenylphosphine molecule we have shown that the AM again is conserved between twisted light and the created exciton, while the average AM of the exciton is found to be zero when the light is polarized perpendicularly to the rotational axis of the molecule, since in this case the light is a linear combination of circularly polarized light with spin 1 and spin -1 .

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