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The angular electronic band structure and free particle model of aromatic molecules: High-frequency photon-induced ring current

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This work introduces an analysis of the relationship of first-principles calculations based on DFT method with the results of free particle model for ring-shaped aromatic molecules. However, the main aim of the study is to reveal the angular electronic band structure of the ring-shaped molecules. As in the case of spherical molecules such as fullerene, it is possible to observe a parabolic dispersion of electronic states with the variation of angular quantum number in the planar ring-shaped molecules. This work also discusses the transition probabilities between the occupied and virtual states by analyzing the angular electronic band structure and the possibility of ring currents in the case of spin angular momentum (SAM) or orbital angular momentum (OAM) carrying light. Current study focuses on the benzene molecule to obtain its angular electronic band structure. The obtained electronic band structure can be considered as a useful tool to see the transition probabilities between the electronic states and possible contribution of the states to the ring currents. The photoinduced current due to the transfer

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of SAM into the benzene molecule has been investigated by using analytical calculations within the frame of time-dependent perturbation theory.

Keywords: Optical angular momentum; electronic excitation; Magnetic moments, theory of electronic structure.

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1. Introduction

For a long time, some exact solutions or numerical and approximate analytical methods have been proposed to solve the Schrödinger equation for the potentials used in quantum mechanics.[1–4] The circularly symmetric or ring-shaped molecules are perfect systems for quantum mechanical applications.[5] Particularly, free electron on a ring-shaped molecule is an example of "particle on a disk" problem and the system can be modeled by infinite radial potential and by using spherical harmonics[6] and spherical Bessel functions. The electronic properties of some ring-shaped clusters have been investigated by using "free particle in an infinite well" model.[7–9] Furthermore, the ring-shaped molecules are good candidates for the application of photoinduced electric currents. The investigation of electric and spin current dynamics has been receiving great attention.[10–12] Not only ring-shaped molecules, but also spherically symmetric or different-shaped molecules have been investigated in the frame of photoinduced current applications.[13,14] Harmonic generation in ring-shaped molecules has also been studied by Ceccherini and Bauer[15] and Ždánská *et al.*[16]

The combination of an analytical model for the radial potential and the first-principles calculations leads to a well-described angular electronic band structure for the spherical molecules.[17–20] Therefore by using this band structure, one can easily see the transition possibilities between the states and analyze the characteristics of the cluster. Inspired by the work of Pavlyukh and Berakdar,[17] we introduce an example of the angular electronic band structure for aromatic molecules. For simplicity, we choose the benzene structure with six carbon and six hydrogen atoms. The number of occupied states are 15 with six π-orbitals. Benzene molecule has a perfect circular geometry and its radial and angular wavefunctions can be described by spherical Bessel function and spherical harmonics, respectively. Although this model lets us to calculate most of the electronic states analytically, it is insufficient to get the true eigenvalues of the so-called π-molecular orbital (MO) states. In principle, orbitals arise from the motion of the π-electrons in the z-direction (perpendicular to the ring plane). But for other states, the motion in z-direction is almost forbidden. Reason for the existence of π-orbitals can be explained by breaking the spherical symmetry.

In this study, we will reveal the differences between the results obtained by first-principles calculations and analytical calculations. Furthermore, the reason of the differences will be explained. The angular electronic band structure of benzene molecule will be introduced. We will present the photoinduced current by circularly polarized light and twisted light and we will discuss the possible contribution of the transitions by investigating the angular electronic band structure. In fact, an analytical expression for the induced current can be obtained by using time-dependent perturbation theory and current density calculations. These calculations can be simplified by using the wavefunctions obtained from the free particle model and "particle on a disk" problem. The current result is compared with those of previous experimental and theoretical studies.

The possibility for production of a persistent current which is produced by a few electrons in a quantum nanostructure has been receiving a great attention due to a couple of reasons. First of all, the persistent current in an ultrasmall quantum system can lead to a strong local magnetic field. Second reason is the possibility of controlling the system by changing the quantum mechanical parameters. Therefore, the simple molecular structures are perfect candidates as tunable quantum mechanical systems for this aim, especially the molecules having the axial or spherical symmetry. The simple and well-known aromatic molecule benzene has an axial symmetry, including some free electrons which are able to circulate around the structure. Its small radius can produce a strong magnetic field in the case of well-circulating electrons with definite magnetic quantum numbers. Exciting the electrons into the preferred magnetic quantum states can exactly be possible by transferring the angular momentum of the so-called optical vortex (twisted light) which is carrying the orbital angular momentum (OAM).

2. Computational Technique

Electronic structure of benzene molecule is calculated by means of Gaussian 09. For optimized structure and electronic structure, we have used density functional theory (DFT) with hybrid B3PW91 functional in conjunction with the 6-311G basis set. The molecular orbital shapes have been obtained by Gauss View 5. Figure 1 shows the molecular π-orbitals obtained by first-principles calculation.

Angular electronic band structure is a result of the solution of Schrödinger equation for a particle in an infinite well potential. The solution has been analytically performed for the π-conjugated system which has been considered as spherically symmetric. In spherical coordinates, the radial Schrödinger equation reads

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V(r)\right] R_{n,\ell}(r) = E_n R_{n,\ell}(r), \tag{1}$$

where radial wavefunction is included in total wavefunction as

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r) Y_{\ell,m}(\theta,\phi). \tag{2}$$

Because the confinement is infinite well potential, in spherical system the radial wavefunction is the spherical Bessel function.

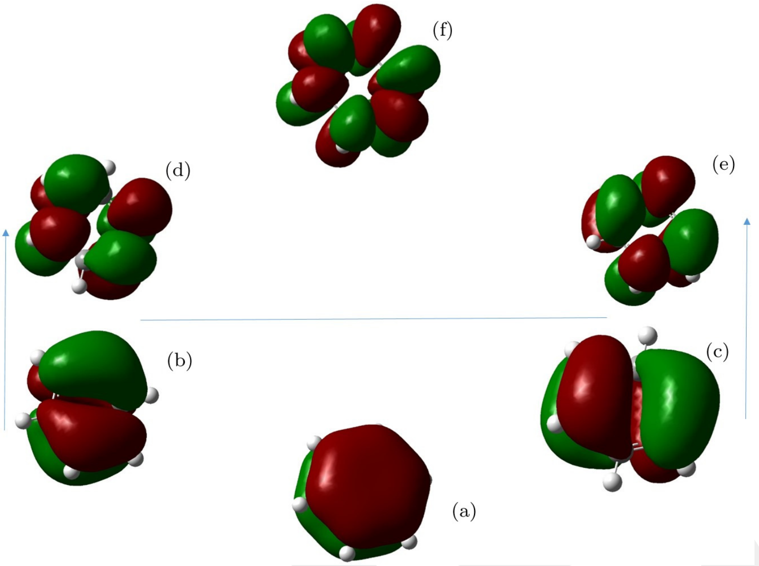


Fig. 1. (Color online) The π-orbitals in benzene molecule. (a) Molecular orbital (MO1) shows the p-state characteristics and the electron density is distributed in z-direction. (b) and (c) Molecular orbitals (MO2 and MO3) resemble the d-state orbitals. (d) and (e) Orbitals MO4 and MO5 correspond to f-state. (f) Orbital (MO6) is g-state orbital. As well known from the UV spectrum, under linearly polarized light beam, the excitation occurs between the shown orbitals in (b) and (c) and the ones in (d) and (e).

3. Angular Electronic Band Structure of C_6H_6

With a perfect ring shape, benzene molecule has six localized and 15 delocalized electronic states. Highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap and radius of the ring are approximately 0.25 Ha and 2.4 a_0 (atomic Bohr radius), respectively. As mentioned in the study of Pavlyukh and Berakdar,[17] the energy levels can be labeled by angular quantum number to obtain the parabolic dispersion of the eigenvalues. This kind of parabolic dispersion for the benzene molecule can be seen in Fig. 2. The figure shows the angular quantum number versus energy levels and corresponding molecular orbitals. One should notice that the angular quantum numbers $\ell = s, p, d, f, g, \ldots$ are denoted by Greek letters: $\lambda = \sigma, \pi, \delta, \phi, \gamma, \ldots$ (Ref. 6).

As seen from Fig. 2, the molecular orbitals are mostly distributed along the xy-plane. These molecular orbital pairs (x-, y-components of same state) are the results of the circular symmetry. Due to the lack of spherical symmetry, the distribution direction and energy value of z-component of the states are quite different when compared with those of x-, y-components. For example, the energy value of π_x- and π_y-states is approximately -0.75 Ha, while the energy value of π_z-state is -0.37 Ha. In order to make a comparison, the molecular orbital shapes of benzene molecule has been shown in Appendix A.

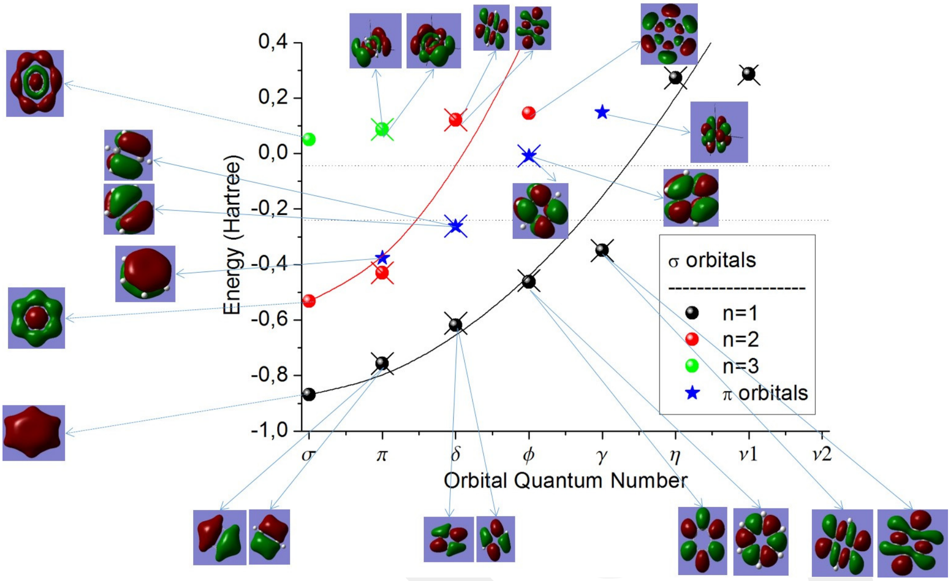


Fig. 2. (Color online) The angular electronic structure of the benzene molecule. The black dots show the energy values for the case of radial quantum number, $n_r = 0$. Dot and cross indicate the x- and y-components of the states, respectively. Red and green dots show the cases of $n_r = 1$ and $n_r = 2$, respectively. Blue dots are π-orbital states which are representing z-component of the states. Because of the circular symmetry, there is not any separation between the x- and y-components of the same states. In order to make sense, in orbital quantum number, π, black dot, black cross and blue star shows x-, y- and z-components of same p-state, respectively.

In order to obtain the eigenvalues and corresponding eigenfunctions of a molecular ring by analytical way, we use the perfect circular symmetry of the benzene and we assume that atoms in the system are located in xy-plane, which is simply the particle on a disc problem.

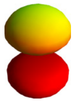
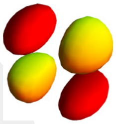
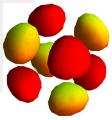
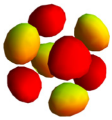
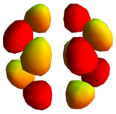
Figure 2 shows the validity of the formula of Pavlyukh and Berakdar[17]:

$$E_{n,\ell} = E_n + \frac{\ell(\ell+1)}{R_n^2}, \tag{3}$$

where n and ℓ are radial quantum number and orbital quantum number, respectively. E indicates the energy level and R_n represents inner/outer radius of molecular rings. Here we assume that the inner radius of molecular rings is $R_{n=1} = 5.29$ a.u. and outer radius is $R_{n=2} = 3.5$ a.u. The π-state energy eigenvalues also have a parabolic trend for which the radius is $R_\pi = 8.1$ a.u. In Fig. 2, one can easily see the transition possibilities between the energy states. Indeed, the transition between π-orbitals or HOMO–LUMO states is in the range of UV-vis spectrum.

Tables 1 and 2 show the shapes of the molecular orbitals obtained by analytical wavefunction formed by combination of Bessel function and spherical harmonics. When compared with the DFT results, it can be easily concluded that they can be used for any physical property of the benzene molecule.

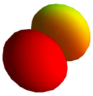
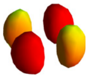
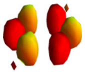
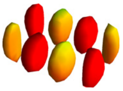
Table 1. The shapes of π molecular orbitals which are obtained by analytical wavefunction formed by combination of Bessel function and spherical harmonics. The molecular orbital shapes have been obtained by calculation of the wavefunction in Eq. (4). When comparing the shapes with those of Fig. 1, it can be concluded that the analytical model is well working for the π-orbitals.

No. of MO	k	Real eigenvalue (Ha)	Analytical wavefunction	Shape
MO1	0.724	−0.3763	$\psi_{2,1,0}(r,\theta,\phi) = N_{2,1}j_1(kr)Y_{1,0}(\theta,\phi)$	
MO2	0.97	−0.261	$\psi_{3,2,\pm1}(r,\theta,\phi) = N_{3,2}j_2(kr)\left[\frac{Y_{2,1}(\theta,\phi)+Y_{2,-1}(\theta,\phi)}{\sqrt{2}}\right]$	
MO3	0.97	−0.261	$\psi_{3,2,\pm1}(r,\theta,\phi) = N_{3,2}j_2(kr)\left[\frac{Y_{2,1}(\theta,\phi)-Y_{2,-1}(\theta,\phi)}{\sqrt{2}}\right]$	
MO4	1.2	−0.00852	$\psi_{4,3,\pm2}(r,\theta,\phi) = N_{4,3}j_3(kr)\left[\frac{Y_{3,2}(\theta,\phi)+Y_{3,-2}(\theta,\phi)}{\sqrt{2}}\right]$	
MO5	1.2	−0.00852	$\psi_{4,3,\pm2}(r,\theta,\phi) = N_{4,3}j_3(kr)\left[\frac{Y_{3,2}(\theta,\phi)-Y_{3,-2}(\theta,\phi)}{\sqrt{2}}\right]$	
MO6	1.434	0.14867	$\psi_{5,4,\pm3}(r,\theta,\phi) = N_{5,4}j_4(kr)\left[\frac{Y_{4,3}(\theta,\phi)+Y_{4,-3}(\theta,\phi)}{\sqrt{2}}\right]$	

As well known from the literature, the possible transition (as expected by UV–vis experiments) can be observed between π-states and as can be seen in Fig. 1, in the case of linearly polarized light beam, the transition will occur between the states shown in Figs. 1(b) and 1(c) and the ones in Figs. 1(d) and 1(e). In this step, we can stop and analyze the π-orbitals following the study of Tai *et al.*.[6] Actually, π-orbitals in benzene molecules are electronic states where the free electrons can circulate around the benzene ring. We can model all molecular orbitals in benzene molecule by using Bessel functions as radial wavefunction and spherical harmonics as angular part of the wavefunction as in the case of Tai *et al.*.[6] Only by changing the radius of the molecule according to the radial quantum number, molecular orbital wavefunction can be written as

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r)Y_{\ell,m}(\theta,\phi), \tag{4}$$

Table 2. The shapes of some occupied molecular orbitals which are obtained by analytical wavefunction formed by combination of Bessel function and spherical harmonics. The molecular orbital shapes have been obtained by calculation of the wavefunction in Eq. (4).

Real eigenvalue (Ha)	Analytical wavefunction	Shape
−0.75707	$\psi_{2,1,1}(r,\theta,\phi) = N_{2,1}j_1(kr)\left[\frac{Y_{1,1}(\theta,\phi)+Y_{1,-1}(\theta,\phi)}{\sqrt{2}}\right]$	
−0.61095	$\psi_{3,2,2}(r,\theta,\phi) = N_{3,2}j_2(kr)\left[\frac{Y_{2,2}(\theta,\phi)+Y_{2,-2}(\theta,\phi)}{\sqrt{2}}\right]$	
−0.45836	$\psi_{4,3,3}(r,\theta,\phi) = N_{4,3}j_3(kr)\left[\frac{Y_{3,3}(\theta,\phi)\pm Y_{3,-3}(\theta,\phi)}{\sqrt{2}}\right]$	
−0.34923	$\psi_{5,4,4;5,2,2}(r,\theta,\phi) = N_{5,4}j_4(kr)\left[\frac{Y_{4,4}(\theta,\phi)-Y_{4,4}(\theta,\phi)}{\sqrt{2}}\right]$ $+ N_{5,2}j_2(kr)\left[\frac{Y_{2,2}(\theta,\phi)-Y_{2,2}(\theta,\phi)}{\sqrt{2}}\right]$	

where n, ℓ, m are radial, orbital and magnetic quantum numbers, respectively. Also r, θ, ϕ are radial position, orbital angle and azimuthal angle, respectively. The radial wavefunction $R_{n,\ell} = Nj_\ell(kr)$ is a spherical Bessel function and N is normalization constant. The k parameter can be found from the equation of $j_\ell(k\rho) = 0$. The radius of benzene ρ is dependent on radial quantum number. Here, one needs to notice that, despite the fact that benzene atoms are located on the xy-plane, we used spherical harmonics to obtain the π-orbitals analytically. Subsequently, in the section of photoinduced current, we use the wavefunction obtained by analytical method and the energy eigenvalues obtained by Gaussian 09. Table 1 shows the analytical wavefunctions obtained from Eq. (4) for six different molecular orbitals.

In the next section analytical wavefunctions and corresponding numerical eigenvalues are used to obtain the possible transitions in the case of spin angular momentum (SAM) transfer to the system (the possibility of OAM transfer will be discussed only in conclusion part). The complete molecular orbital states obtained by DFT calculation can be seen in Appendix A.

4. Possible Transitions and Ring Current in Benzene Molecule by SAM Transfer of Photon

According to the transition rule, in the case of linearly x- or y-polarized light, transition occurs when $\Delta m = \pm 1$ and $\Delta \ell = 1$. In the range of UV–vis spectrum, experiments show that absorption peak for the benzene molecule is approximately at 0.26 Ha, and according to the DFT calculations on benzene molecule this peak has been resulted from the transition between MO20 and MO21 and between MO22 and MO23 (π-orbitals) of which the molecular orbital shapes can be seen in Appendix A.

Circular polarization of the light leads to the jumping of the occupied-state electrons to the virtual states which have the net magnetic quantum number. Net magnetic quantum number causes production of photoinduced current. In this section, the transition matrix elements and induced current for benzene molecule will be calculated by using analytical wavefunction which have been shown in Tables 1 and 2 and energy eigenvalues obtained by DFT calculation. The current density for the right and left circular polarized light can be written as follows:

$$I(\omega = (\omega_{k,k'} - \omega_{k_0}), t = 0) = \frac{i}{2}\frac{4}{\delta^2}\sum_{k=22}^{27}\sum_{k'=22}^{27}\langle k_0|e^{\pm i\phi}|k\rangle\langle k_0|e^{\pm i\phi}|k'\rangle^* M_{k,k'}, \qquad (5)$$

where ω is the frequency of electromagnetic radiation that interacted with the molecule and ω is equal to the difference between the energy of excited state, $\omega_{k,k'}$, and the energy of ground state, $\omega_{k_0} \cdot \delta$ is a measure of the transition time. k_0, k, k' indicate indices of ground and excited states. $M_{k,k'}$ is giving the possibility of current which reads

$$M_{k,k'} = \int_0^R \int_0^\pi \int_0^{2\pi} (\psi_k \nabla \psi_{k'}^* - \psi_{k'}^* \nabla \psi_k) \sin\theta r^2 d\theta d\phi dr. \qquad (6)$$

Equation (5) includes the transition probability values $\langle k_0|e^{\pm i\phi}|k\rangle$ and $\langle k_0|e^{\pm i\phi}|k'\rangle^*$ which have the explicit forms as

$$\begin{aligned}\langle k_0|e^{\pm i\phi}|k\rangle &= \int \psi_{k_0}(\mathbf{r}) e^{\pm i\phi}\psi_k^*(\mathbf{r})d\mathbf{r},\\ \langle k_0|e^{\pm i\phi}|k'\rangle^* = \langle k'|e^{\mp i\phi}|k_0\rangle &= \int \psi_{k_0}^*(\mathbf{r}) e^{\mp i\phi}\psi_{k'}(\mathbf{r})d\mathbf{r}.\end{aligned} \qquad (7)$$

The numerical results of integration of matrix elements and transition energy can be seen in Table 3, where six different transition probabilities have been indicated. The first indices indicate the occupied electronic states and second indices show the

Table 3. The numerical results of $\langle k_0|e^{i\phi}|k\rangle$ for right (+) circular polarized light.

$\frac{\text{LUMO}}{\text{HOMO}}$	22	23	24	26	27	$\omega_k - \omega_{k_0}$
7	0	0	0	−0.0448824	−0.0448824	0.95562 Ha
8	0	0	0.248733	0	0	0.8071 Ha
9	0	0	−0.248733	0	0	0.8071 Ha
10	0	0	0	−0.161967	0.161967	0.696 Ha
11	0	0	0	0.161967	−0.161967	0.696 Ha
12	0	0	0	−0.1	−0.1	0.619 Ha
15	0	0	−0.57951	0	0	0.46973 Ha
16	0	0	0.57951	0	0	0.46973 Ha
18	0	0	0	0.103944	−0.103944	0.436 Ha
19	0	0	0	0.103944	−0.103944	0.436 Ha
20	−0.115334	−0.115334	0	0	0	0.25285 Ha
21	−0.115334	−0.115334	0	0	0	0.25285 Ha

excited and unoccupied states. The numerical values of photoinduced current for different frequencies can be written as

$$\begin{aligned}
\omega &= 0.95562\ \text{Ha}; \quad I = A_0^2 7.62451\hat{\phi}\,,\\
\omega &= 0.696\ \text{Ha}; \quad I = -A_0^2 198.584\hat{\phi}\,,\\
\omega &= 0.619\ \text{Ha}; \quad I = A_0^2 38.2186\hat{\phi}\,,\\
\omega &= 0.436\ \text{Ha}; \quad I = -A_0^2 81.7878\hat{\phi}\,,\\
\omega &= 0.25285\ \text{Ha}; \quad I = A_0^2 173.398\hat{\phi}\,,
\end{aligned} \tag{8}$$

where the field strength A_0 will affect the result of the current. If we choose the field strength as 7.3×10^{-5} a.u. $= 3.75 \times 10^{7}$ V/m as in the case of study of Nobusada and Yabana,[10] the current for $\omega = 0.25285$ Ha will be 4.7 nA (in the study of Nobusada and Yabana, this value was 7 nA). The difference between our study and Ref. 10 is that we performed our calculations by using analytical wavefunctions. Indeed, this agreement indicates that the analytical wavefunctions are sufficient to model the system and to find out the physical properties. The results in Eq. (8) show that the magnitude and direction of current are varying with the change in frequency.

5. Conclusion

We studied the angular electronic band structure of the benzene molecule and possible transitions in the case of SAM carrying light. We demonstrate that the photoinduced current can be calculated by using analytical wavefunction and real eigenvalues. The current is directly dependent on the transfer of the light angular momentum to the system. We also revealed that the high-frequency transitions in benzene molecule can lead to the photoinduced current.

Furthermore, the results in Eq. (8) show that the transitions in the case of right circular polarized light lead to the transitions into virtual molecular states with negative sign or positive sign magnetic quantum number. This means that the photoinduced current direction changes with the variation of frequency. The change in the frequency causes a variation of the magnitude of the current and change of the direction of the current. For large molecular clusters, it might be possible to observe a change in the current direction with a sensitive tuning of the frequency of the light for one-direction circular polarized light.

In the case of OAM transfer, the topological charge will be definitive for the transitions between the states. OAM carrying light (e.g., Laguerre–Gaussian beam) has a spatial distribution and generally beam waist is in μm scale. On the other hand, following the studies of Quinteiro and Kuhn,[21] we can assume that the light is highly focused and the beam waist is in nm scale. The advantage of the OAM carrying light is the possibility of increasing the number of electrons which would contribute to the photoinduced current, but OAM transfer is outside the scope of the current paper.

Acknowledgments

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Appendix A

In Tables A.1 and A.2, we also show all molecular orbital states obtained by Gaussian 09 software using the density functional theory with hybrid B3PW91 functional in conjunction with the 6-311G basis set.

Table A.1. HOMO states of benzene molecule. Here, "$*$" indicates the π-orbital states and "$+$" indicates the hybrid orbitals.

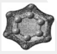
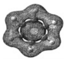
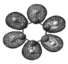
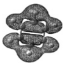
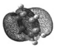
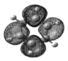
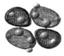
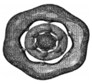
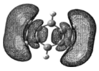
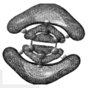
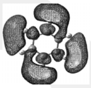
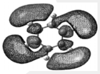
State	No. of MO	Label	E (Ha)	Shape
HOMO−14	MO7	1σ	−0.86875	
HOMO−13	MO8	$1\pi_x$	−0.75707	
HOMO−12	MO9	$1\pi_y$	−0.75703	
HOMO−11	MO10	$1\delta_x$	−0.61095	
HOMO−10	MO11	$1\delta_y$	−0.61090	
HOMO−9	MO12	2σ	−0.53231	
HOMO−8	MO13	$1\phi_x$	−0.45836	
HOMO−7	MO14	$1\phi_y$	−0.46279	
HOMO−6	MO15	$2\pi_x$	−0.4297	
HOMO−5	MO16	$2\pi_y$	−0.42969	
HOMO−4	MO17	$1\sigma^*$	−0.3763	
HOMO−3	MO18	$1\gamma_x - 2\delta_x^+$	−0.34923	
HOMO−2	MO19	$1\gamma_y - 2\delta_y^+$	−0.34916	
HOMO−1	MO20	$1\pi_x^*$	−0.26141	
HOMO	MO21	$1\pi_y^*$	−0.26137	

Table A.2. LUMO states of benzene molecule. Here, "$*$" indicates the π-orbital states.

State	No. of MO	Label	E (Ha)	Shape
LUMO	MO22	$1\delta_x^*$	-0.00852	
LUMO+1	MO23	$1\delta_y$	-0.00846	
LUMO+2	MO24	3σ	0.05003	
LUMO+3	MO25	$3\pi_x$	0.08687	
LUMO+4	MO26	$3\pi_y$	0.08687	
LUMO+5	MO27	$2\delta_x$	0.12157	
LUMO+6	MO28	$2\delta_y$	0.12157	
LUMO+7	MO29	$2\phi_x$	0.14526	
LUMO+8	MO30	$1\phi_x^*$	0.14867	

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