Control of $p$-Electron Rotation in Chiral Aromatic Molecules by Nonhelical Laser Pulses

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A. Procedure for calculating eigenstates of the PPP Hamiltonian $\hat{H}_x$

The PPP Hamiltonian $\hat{H}_x$ is reduced to the Hückel Hamiltonian $\hat{H}_{\text{HMO}}$ by setting Coulomb repulsion terms to zero. In order to obtain eigenstates of $\hat{H}_x$, we first calculate those of $\hat{H}_{\text{HMO}}$. Orbital energies and LCAO coefficients of eight $p$-orbitals of 2,5-dichloro[6](3,6)pyrazinophane (DCP), $|1_{a_u}\rangle$, $|1_{b_g}\rangle$, $|2_{a_u}\rangle$, $|2_{b_g}\rangle$, $|3_{b_g}\rangle$ (HOMO), $|3_{a_u}\rangle$ (LUMO), $|4_{a_u}\rangle$, and $|4_{b_g}\rangle$ (in ascending order of orbital energy), are obtained by solving the secular equation. An eigenstate of $\hat{H}_{\text{HMO}}$ is represented by the Slater determinant composed of the LCAO-MOs. Configuration interaction is then taken into account by diagonalizing $\hat{H}_x$ including all singlet single and double excitations (SDCI). Consequently, 136 singlet eigenstates of $\hat{H}_x$, each of which is a linear combination of those of $\hat{H}_{\text{HMO}}$, are obtained by SDCI using 15 single and 120 double excitations. Table A1 shows the results of the SDCI calculation of DCP.
Table A1: Properties of optically-allowed \( p \)-electronic excited states whose transition energies are less than 10.0 eV. Weight is a square of a CI coefficient of each electronic configuration.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Transition energy / eV</th>
<th>Oscillator strength</th>
<th>Dominant electronic configurations</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>1\rangle=</td>
<td>1^1B_u\rangle)</td>
<td>4.31</td>
<td>3.46 (\times) 10(^{-1})</td>
</tr>
<tr>
<td>(</td>
<td>2\rangle=</td>
<td>2^1B_u\rangle)</td>
<td>5.05</td>
<td>8.52 (\times) 10(^{-2})</td>
</tr>
<tr>
<td>(</td>
<td>4\rangle=</td>
<td>3^1B_u\rangle)</td>
<td>6.66</td>
<td>1.00</td>
</tr>
<tr>
<td>(</td>
<td>7\rangle=</td>
<td>4^1B_u\rangle)</td>
<td>7.07</td>
<td>1.05</td>
</tr>
<tr>
<td>(</td>
<td>9\rangle=</td>
<td>5^1B_u\rangle)</td>
<td>7.66</td>
<td>2.31</td>
</tr>
<tr>
<td>(</td>
<td>10\rangle=</td>
<td>6^1B_u\rangle)</td>
<td>7.77</td>
<td>1.51</td>
</tr>
<tr>
<td>(</td>
<td>15\rangle=</td>
<td>7^1B_u\rangle)</td>
<td>9.79</td>
<td>2.29 (\times) 10(^{-3})</td>
</tr>
</tbody>
</table>

\([a]\) This double excitation consists of a singlet electron pair and a singlet hole pair.\(^{[2]}\)

B. Definition of the momentum operator \( \hat{p} \)

Complex MOs \( \{\psi_j\} \) of an aromatic molecule of \( D_{Mn} \) symmetry are given by

\[
\psi_j = \frac{1}{M^{1/2}} \sum_{m=1}^M \exp\left(i \frac{2j\pi}{M} m\right) \chi_m, \tag{B1}
\]

where \( M \) denotes the number of atoms in the aromatic ring, e.g., \( M = 6 \) for benzene, and \( \chi_m \) is a \( p_z \)-orbital at the \( m \)th atom. The integer \( j \) reads \( j = -M/2+1,...,0,...,M/2 \). By approximating a polygonal structure of the molecule with a complete cylindrical ring, the complex MO \( \psi_j \) can be regarded as a traveling wave with the momentum \( \hat{p}_j \) for a circular path along the ring:\(^{[3]}\)

\[
\hat{p}_j = \begin{cases} 
 jh/b & (1 \leq |j| \leq M/2 - 1) \\
 0 & (j = 0, M/2)
\end{cases}, \tag{B2}
\]
where $b$ is the radius of the ring. The momentum operator $\hat{p}$ is defined as

$$\hat{p} = \sum_{j, \sigma} p \hat{\gamma}_{j, \sigma},$$

(B3)

where $\hat{\gamma}_{j, \sigma}$ is the number operator of $p$-electrons with a spin $s$ occupying $|\psi_j\rangle$. The expectation value $p(t) \equiv \langle \Psi(t)|\hat{p}|\Psi(t)\rangle$ is then calculated by additions and multiplications of LCAO coefficients, CI coefficients, phase factors $\{e^{-iE_s t/\hbar}\}$, and expansion coefficients $\{c_k(t)\}$.

$p$-Electrons with a nonzero value of $p_j$ circulate around the ring with radius $b$. Hence, angular momentum of $p$-electrons occupying $|\psi_j\rangle$ is simply given by $\ell_j = bp_j$, and the angular momentum operator is expressed as $\hat{\ell} = b\hat{p}$.

C. Transformation of phase factors

The expansion of $|\Psi(t)\rangle$ can be rewritten as

$$|\Psi(t)\rangle = e^{-iE_0 t/\hbar} \sum_k c_k(t) e^{-i(E_k - E_0) t/\hbar} |k\rangle.$$  

(C1)

The global phase factor $e^{-iE_0 t/\hbar}$ at the forefront of the right-hand side of Equation (C1) is cancelled when one calculates populations of each electronic state or expectation values of any physical quantity. Therefore, the phase factor for $|k\rangle$ is transformed into $e^{-(E_k - E_0) t/\hbar}$, and after excitation from $|0\rangle$ to $|9\rangle \pm |10\rangle$ at $t = t_1$, $|10\rangle$ is multiplied by $e^{-i\phi(t)}$, where $\phi(t) = 2\Delta E(t - t_1) / \hbar$ and $2\Delta E \equiv E_{10} - E_0$.

If the global phase factor is chosen as $e^{-iE_0 t/\hbar}$, $|\Psi(t)\rangle$ can be expanded as

$$|\Psi(t)\rangle = e^{-iE_0 t/\hbar} \sum_k c_k(t) e^{-i(E_k - E_0) t/\hbar} |k\rangle.$$  

(C2)

The summations in Equations (C1) and (C2) are quantum mechanically equivalent to each other since $e^{-iE_0 t/\hbar}$ in Equation (C2) is also cancelled for expectation values of any physical quantity. Thus, the model analysis in the text is independent of the choice of the global phase factor.

References