Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# ELECTRONIC SUPPLEMENTARY INFORMATION:

# Partition of Optical Properties Into Orbital Contributions

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## S.I. PNOC EXPRESSIONS FOR NLOPS

The transformation matrix C corresponds to the change between atomic orbitals (AOs) and natural orbitals (NOs)

$$\chi^{NO} = \phi^{AO}\mathbf{C} \tag{1}$$

where $\chi^{NO}$ and $\phi^{AO}$ are row vectors, and the linear combination of atomic orbitals (LCAO) coefficients $\mathbf{C}$ are organized in the columns of $\mathbf{C}$. This matrix is used to obtain the projection from AOs basis to NOs basis within the first-order reduced density matrix (1-RDM) representation of NLOPs:

$$\begin{aligned}\alpha_{ij} &= -\sum_{\mu\nu} D^{(j)}_{\mu\nu} h^{(i)}_{\nu\mu} = -\mathrm{Tr}(\mathbf{D}^{(j)}\mathbf{h}^{(i)}) \\ &= -\mathrm{Tr}(\mathbf{C}^{-1}\mathbf{D}^{(j)}(\mathbf{C}^{-1})^{\dagger}\mathbf{C}^{\dagger}\mathbf{h}^{(i)}\mathbf{C}) \\ &= -\mathrm{Tr}(\mathbf{\Delta}^{(j)}\mathbf{M}^{(i)}) = -\sum_{pq} \Delta^{(j)}_{pq} M^{(i)}_{qp}\end{aligned} \tag{2}$$

$$\begin{aligned}\beta_{ijk} &= -\sum_{\mu\nu} D^{(jk)}_{\mu\nu} h^{(i)}_{\nu\mu} = -\mathrm{Tr}(\mathbf{D}^{(jk)}\mathbf{h}^{(i)}) \\ &= -\mathrm{Tr}(\mathbf{C}^{-1}\mathbf{D}^{(jk)}(\mathbf{C}^{-1})^{\dagger}\mathbf{C}^{\dagger}\mathbf{h}^{(i)}\mathbf{C}) \\ &= -\mathrm{Tr}(\mathbf{\Delta}^{(jk)}\mathbf{M}^{(i)}) = -\sum_{pq} \Delta^{(jk)}_{pq} M^{(i)}_{qp}\end{aligned} \tag{3}$$

$$\begin{aligned}\gamma_{ijkl} &= -\sum_{\mu\nu} D^{(jkl)}_{\mu\nu} h^{(i)}_{\nu\mu} = -\mathrm{Tr}(\mathbf{D}^{(jkl)}\mathbf{h}^{(i)}) \\ &= -\mathrm{Tr}(\mathbf{C}^{-1}\mathbf{D}^{(jkl)}(\mathbf{C}^{-1})^{\dagger}\mathbf{C}^{\dagger}\mathbf{h}^{(i)}\mathbf{C}) \\ &= -\mathrm{Tr}(\mathbf{\Delta}^{(jkl)}\mathbf{M}^{(i)}) = -\sum_{pq} \Delta^{(jkl)}_{pq} M^{(i)}_{qp}\end{aligned} \tag{4}$$

where $\mathbf{M}^{(i)}$ is the transition dipole matrix and $\mathbf{\Delta}^{(j_1 \cdots j_n)}$ is the $n$-order derivative of the 1-RDM with respect to field in the directions $j_1 \ldots j_n$ calculated in the NO basis:

$$\mathbf{M}^{(i)} = \mathbf{C}^{\dagger}\mathbf{h}^{(i)}\mathbf{C} \tag{5}$$

$$\mathbf{\Delta}^{(j)} = \mathbf{C}^{-1}\mathbf{D}^{(j)}(\mathbf{C}^{-1})^{\dagger} \tag{6}$$

$$\mathbf{\Delta}^{(jk)} = \mathbf{C}^{-1}\mathbf{D}^{(jk)}(\mathbf{C}^{-1})^{\dagger} \tag{7}$$

$$\mathbf{\Delta}^{(jkl)} = \mathbf{C}^{-1}\mathbf{D}^{(jkl)}(\mathbf{C}^{-1})^{\dagger} \tag{8}$$

The latter expression can be further developed to obtain the contribution of orbital $p$ to the corresponding NLOP:

$$\alpha_{ij} = -\sum_{pq} \Delta^{(j)}_{pq} M^{(i)}_{qp} = \sum_{p} \alpha_{ij,p} \tag{9}$$

$$\begin{aligned}\alpha_{ij,p} &= -\Delta^{(j)}_{pp} M^{(i)}_{pp} - \frac{1}{2} \sum_{q \neq p} \left( \Delta^{(j)}_{pq} M^{(i)}_{qp} + \Delta^{(j)}_{qp} M^{(i)}_{pq} \right) \\ &= -\Delta^{(j)}_{pp} M^{(i)}_{pp} - \sum_{q \neq p} \Delta^{(j)}_{pq} M^{(i)}_{pq} \end{aligned} \tag{10}$$

$$\beta_{ijk} = -\sum_{pq} \Delta^{(jk)}_{pq} M^{(i)}_{qp} = \sum_{p} \beta_{ijk,p} \tag{11}$$

$$\begin{aligned}\beta_{ijk,p} &= -\Delta^{(jk)}_{pp} M^{(i)}_{pp} - \frac{1}{2} \sum_{q \neq p} \left( \Delta^{(jk)}_{pq} M^{(i)}_{qp} + \Delta^{(jk)}_{qp} M^{(i)}_{pq} \right) \\ &= -\Delta^{(jk)}_{pp} M^{(i)}_{pp} - \sum_{q \neq p} \Delta^{(jk)}_{pq} M^{(i)}_{pq} \end{aligned} \tag{12}$$

$$\gamma_{ijk} = -\sum_{pq} \Delta^{(jkl)}_{pq} M^{(i)}_{qp} = \sum_{p} \gamma_{ijkl,p} \tag{13}$$

$$\begin{aligned}\gamma_{ijkl,p} &= -\Delta^{(jkl)}_{pp} M^{(i)}_{pp} - \frac{1}{2} \sum_{q \neq p} \left( \Delta^{(jkl)}_{pq} M^{(i)}_{qp} + \Delta^{(jkl)}_{qp} M^{(i)}_{pq} \right) \\ &= -\Delta^{(jkl)}_{pp} M^{(i)}_{pp} - \sum_{q \neq p} \Delta^{(jkl)}_{pq} M^{(i)}_{pq} \end{aligned} \tag{14}$$

Equations 10, 12 and 14 represent the contribution of orbital $p$ to the polarizability, the first- and the second-hyperpolarizability, respectively. This analysis can be straightforwardly extended to high-order properties.

## S.II. ORIGIN–DEPENDENCY IN PNOC

In PNOC, the origin–dependency comes directly from the $\mathbf{M}^{(i)}$ matrix and can affect the orbital contributions to the optical properties. For example, the $\alpha_{ii,p}$ component upon translation of the system by a vector $T_i$ can be evaluated as:

$$\begin{aligned}\alpha_{ii,p}(T_i) &= -\Delta^{(j)}_{pp} \langle \chi_p \mid r_i - T_i \mid \chi_p \rangle - \sum_{q \neq p} \Delta^{(j)}_{pq} \langle \chi_p \mid r_i - T_i \mid \chi_q \rangle \\ &= \alpha_{ii,p}(\mathbf{0}) + T_i \Delta^{(j)}_{pp} \end{aligned}$$

where we assumed the orthonormality of the NOs, $\langle \chi_p \mid \chi_q \rangle = \delta_{pq}$. In this work, we have assumed that the origin axis is fixed at the center of mass.

For systems centrosymmetric along the studied axis $i$, all diagonal matrix elements $D_{pp}^{(i)}$ are equal to zero (same holds for higher odd derivatives). In such cases, this property makes PNOC free of the origin–dependency problem and supports its usage in the analysis especially of the $\alpha_{ii}$ and $\gamma_{iiii}$ components (in such systems $\beta_{iii}$ vanishes).

## S.III. NUMERICAL DIFFERENTIATION OF 1-RDMS

The 1-RDM derivatives were obtained using numerical differentiation of each matrix element separately. For computing the elements of $\mathbf{D}^{(j)}$, $\mathbf{D}^{(jj)}$ and $\mathbf{D}^{(jjj)}$, central differences formula utilizing 4–, 5– and 6–points were used:[1]

$$\begin{aligned}
D_{\mu\nu}^{(j)} =& \frac{1}{12F_j}\left[D_{\mu\nu}(-2F_j) - 8D_{\mu\nu}(-F_j)\right. \\
& \left. +8D_{\mu\nu}(F_j) - D_{\mu\nu}(2F_j)\right] \qquad (15) \\
D_{\mu\nu}^{(jj)} =& \frac{1}{12F_j^2}\left[-D_{\mu\nu}(-2F_j) + 16D_{\mu\nu}(-F_j)\right. \\
& \left. -30D_{\mu\nu}(0) + 16D_{\mu\nu}(F_j) - D_{\mu\nu}(2F_j)\right] \qquad (16) \\
D_{\mu\nu}^{(jjj)} =& \frac{1}{48F_j^3}\left[D_{\mu\nu}(-4F_j) - 34D_{\mu\nu}(-2F_j) + 64D_{\mu\nu}(-F_j)\right. \\
& \left. -64D_{\mu\nu}(F_j) + 34D_{\mu\nu}(2F_j) - D_{\mu\nu}(4F_j)\right] \qquad (17)
\end{aligned}$$

These expressions provide total values of NLOPs consistent with the ones obtained from the analogous differentiation of total energies in the same manner. The numerical accuracy of Eqs. 15-17 (using $F_j$=0.002 a.u.) was tested against the Romberg-Rutishauser iterative differentiation scheme of the total electronic energies (using a minimal value of $F_j$=0.0005 a.u.), which successfully reduces the truncation errors coming from higher derivatives.[2,3] The errors committed in the total value of NLOP (obtained as the sum of PNOC contributions) were below 0.01% in $\alpha_{zz}$ and 0.5% in $\gamma_{zzzz}$.

## S.IV. ORBITAL PARTITIONING WITHIN SUM–OVER–STATES

The results of the PNOC scheme have been compared with the results obtained with sum–over–states (SOS), which is the most common method to analyze the nature of the electronic response. Within the SOS formalism, $\alpha_{ii}^{\mathrm{SOS}}$ and $\gamma_{iiii}^{\mathrm{SOS}}$ are defined as:

$$\alpha_{ii}^{\mathrm{SOS}} = -2 \sum_{m\neq 0} \frac{\mu_{0m}\mu_{m0}}{E_0 - E_m} \tag{18}$$

$$\begin{aligned}\gamma_{iiii}^{\mathrm{SOS}} &= -24 \sum_{m\neq 0}\sum_{n\neq 0}\sum_{s\neq 0} \frac{\mu_{0n}(\mu_{nm} - \delta_{nm}\mu_{00})(\mu_{ms} - \delta_{ms}\mu_{00})\mu_{s0}}{(E_0 - E_n)(E_0 - E_m)(E_0 - E_s)} \\ &\quad + 24 \sum_{m\neq 0} \frac{\mu_{0m}\mu_{m0}}{(E_0 - E_m)} \sum_{n\neq 0} \frac{\mu_{0n}\mu_{n0}}{(E_0 - E_n)^2}\end{aligned} \tag{19}$$

where $\mu_{mn} = \langle \Psi_m \mid \hat{\mu}_i \mid \Psi_n \rangle$ is the $i$–th component of the transition dipole moment between two states $\Psi_m$ and $\Psi_n$, $E_m$ is the energy of the $m$–th state, and $i \in \{x, y, z\}$.

The SOS definition of the NLOPs is a true representation of the *coupled* response only if the (complete) set of the unperturbed wavefunctions $\{\Psi_m\}$ are the eigenfunctions of the exact Hamiltonian of the unperturbed system.[4,5] For many–electron systems this is fulfilled only by the full-configuration interaction (FCI) method. In the case of other electronic structure methods providing information on the excited states, such as configuration interaction singles (CIS) or time-dependent Hartree-Fock (TDHF), the SOS expressions yield approximate *uncoupled* values of the NLOPs.[5–11]

A popular variant of the SOS is uncoupled Hartree–Fock (UCHF),[8] which employs the eigenvalue and eigenfunctions of the non-interacting Hamiltonian (*i.e.*, the exact field-free Hamiltonian of the system minus the electron-electron operator). Owe to the Slater–Condon rules for single–determinant wavefunctions, the one–particle operator term $\langle \Psi_0 \mid \hat{\mu}_i \mid \Psi_m \rangle$ is non–zero only for single–excitation excited states. Therefore, the UCHF expression for $\alpha_{zz}^{\mathrm{UCHF}}$ and $\gamma_{zzzz}^{\mathrm{UCHF}}$ is:[8]

$$\alpha_{zz}^{\mathrm{UCHF}} = -4\sum_{p}^{occ}\sum_{a}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_p\rangle}{\varepsilon_p - \varepsilon_a} \tag{20}$$

$$\begin{aligned}
\gamma_{zzzz}^{\mathrm{UCHF}} - 24 \Bigg[ & 2\sum_{p,q,r}^{occ}\sum_{a}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_r\rangle\langle\phi_r \mid \hat{\mu}_z \mid \phi_q\rangle\langle\phi_q \mid \hat{\mu}_z \mid \phi_p\rangle}{(\varepsilon_p - \varepsilon_a)(\varepsilon_q - \varepsilon_a)(\varepsilon_r - \varepsilon_a)} \\
& -2\sum_{p,q}^{occ}\sum_{a,c}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_c\rangle\langle\phi_c \mid \hat{\mu}_z \mid \phi_q\rangle\langle\phi_q \mid \hat{\mu}_z \mid \phi_p\rangle}{(\varepsilon_p - \varepsilon_a)(\varepsilon_q - \varepsilon_a)(\varepsilon_q - \varepsilon_c)} \\
& -2\sum_{p,r}^{occ}\sum_{a,b}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_b\rangle\langle\phi_b \mid \hat{\mu}_z \mid \phi_r\rangle\langle\phi_r \mid \hat{\mu}_z \mid \phi_p\rangle}{(\varepsilon_p - \varepsilon_a)(\varepsilon_p - \varepsilon_b)(\varepsilon_r - \varepsilon_b)} \\
& +2\sum_{p}^{occ}\sum_{a,b,c}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_b\rangle\langle\phi_b \mid \hat{\mu}_z \mid \phi_c\rangle\langle\phi_c \mid \hat{\mu}_z \mid \phi_p\rangle}{(\varepsilon_p - \varepsilon_a)(\varepsilon_p - \varepsilon_b)(\varepsilon_p - \varepsilon_c)} \\
& -2\sum_{p,q}^{occ}\sum_{a,b}^{vir}\frac{\langle\phi_p \mid \hat{\mu}_z \mid \phi_a\rangle\langle\phi_a \mid \hat{\mu}_z \mid \phi_q\rangle\langle\phi_q \mid \hat{\mu}_z \mid \phi_b\rangle\langle\phi_b \mid \hat{\mu}_z \mid \phi_p\rangle}{(\varepsilon_p - \varepsilon_a)(\varepsilon_p - \varepsilon_b)(\varepsilon_q - \varepsilon_a)}\Bigg]
\end{aligned} \tag{21}$$

where the $p$, $q$, $r$ indices run over doubly occupied molecular orbitals (MOs), the $a$, $b$, $c$ indices run over virtual molecular orbitals, and $\phi_p$ and $\varepsilon_p$ are $p$–th canonical MO and its energy, respectively. UCHF is known to underestimate the coupled values of NLOPs. For polarizabilities, the errors are usually about 20-40%, whereas for first and second hyperpolarizabilities the errors can be as large as 80%-100% (or even larger).[6,8,10,12]

SOS represents the response to the external field in terms of dipole allowed transitions between the states. However, it is possible to express it in terms of the orbitals involved in the transitions. For example, in UCHF, the contribution of a particular term in the Eq. 20 can be equally divided between $\phi_p$ and $\phi_a$ molecular orbitals. In the case of FCI, the wavefunction is no longer a one-Slater determinant and, the restriction to single excitations holds no more. However, an approximate partitioning of $\alpha_{zz}^{\mathrm{SOS}}$ can be done if one assumes that the character of NOs does not change significantly during the transition to energetically higher states. Then, one can distribute the single summation term of Eq. 18 (related to the transition from the ground state to the $m$–th excited state) into $\alpha_{zz,p}^{\mathrm{SOS}}$ NO contributions, using the weights $w_{p,m}$ defined by changes of the occupancy $n_p$ of $p$–th NO during the transition from $\Psi_0$ ($n_{p,0}$) to $\Psi_m$ ($n_{p,m}$):

$$\alpha_{zz,p}^{\mathrm{SOS}} = -2\sum_{m} w_{p,m}\frac{\mu_{0m}\mu_{m0}}{E_0 - E_m} \tag{22}$$

$$w_{p,m} = \frac{|n_{p,m} - n_{p,0}|}{\sum_q |n_{q,m} - n_{q,0}|} \tag{23}$$

where $\mu_{m0}$ and $E_m$ are defined in Eqs. 18 and 19. For CIS or TDHF, the same partitioning can be adapted using a different definition for the weights ($w_{p,m}^{\mathrm{CIS/TDHF}}$) involving the square of the coefficients of the single excitations $\phi_p \to \phi_q$ in which the molecular orbital $\phi_p$ is involved ($c_{pq}^{m}$):

$$w_{p,m}^{\mathrm{CIS/TDHF}} = \frac{1}{2}\sum_{q\neq p}\left(c_{pq}^{m}\right)^2 \tag{24}$$

In the case of the components of higher–order NLOPs (*e.g.*, $\gamma_{zzzz}$), such SOS partitioning is also possible, however, due to the high inaccuracy of the uncoupled approximation, further decomposition is, at the very least, questionable. Therefore, in our analysis we have focused only on the SOS orbital contributions to $\alpha_{zz}$.

## S.V. SUPPLEMENTARY TABLES

TABLE S.I. Comparison between the orbital contributions to $\alpha_{zz}$ in $(H_2)_3$ obtained from the SOS and the PNOC schemes. For each particular method, the absolute values (in a.u.) of the NOs contributions to $\alpha_{zz}$ are presented (relative contributions given in parentheses). All methods employed the cc–pVDZ basis set.

| NO | SOS(UCHF) | SOS(TDHF) | PNOC(RHF) | SOS(FCI) | PNOC(FCI) |
|---|---|---|---|---|---|
| $1\sigma_g^+$ | 0.54 (1.5%) | 0.39 (0.7%) | 0.87 (1.6%) | 0.39 (0.8%) | 0.85 (1.7%) |
| $1\sigma_u^+$ | 2.72 (7.4%) | 2.18 (3.9%) | 4.40 (7.9%) | 1.74 (3.5%) | 4.04 (8.0%) |
| $2\sigma_g^+$ | 15.01 (41.1%) | 25.32 (45.4%) | 22.64 (40.6%) | 22.66 (45.1%) | 19.91 (39.5%) |
| $2\sigma_u^+$ | 14.96 (41.0%) | 25.47 (45.7%) | 22.60 (40.5%) | 22.63 (45.0%) | 17.48 (34.7%) |
| $3\sigma_g^+$ | 2.66 (7.3%) | 2.14 (3.8%) | 4.39 (7.9%) | 1.41 (2.8%) | 3.17 (6.3%) |
| $3\sigma_u^+$ | 0.48 (1.3%) | 0.20 (0.4%) | 0.87 (1.6%) | 0.49 (1.0%) | 0.71 (1.4%) |
| Sum $\sigma$(FV) | 36.38 (99.6%) | 55.70 (99.9%) | 55.75 (99.9%) | 49.30 (98.1%) | 46.15 (91.6%) |
| $4\sigma_g^+$ | 0.00 (0.0%) | 0.01 (0.0%) | 0.00 (0.0%) | 0.22 (0.4%) | 0.14 (0.3%) |
| $4\sigma_u^+$ | 0.04 (0.1%) | 0.02 (0.0%) | 0.01 (0.0%) | 0.17 (0.3%) | 0.21 (0.4%) |
| $5\sigma_g^+$ | 0.03 (0.1%) | 0.02 (0.0%) | 0.00 (0.0%) | 0.11 (0.2%) | 0.27 (0.5%) |
| $5\sigma_u^+$ | 0.05 (0.1%) | 0.01 (0.0%) | 0.01 (0.0%) | 0.14 (0.3%) | 1.75 (3.5%) |
| $6\sigma_g^+$ | 0.02 (0.1%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.00 (0.0%) | 0.51 (1.0%) |
| $6\sigma_u^+$ | 0.01 (0.0%) | 0.01 (0.0%) | 0.00 (0.0%) | 0.02 (0.0%) | 0.20 (0.4%) |
| $7\sigma_g^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.07 (0.1%) | 0.14 (0.3%) |
| $7\sigma_u^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.05 (0.1%) | 0.51 (1.0%) |
| $8\sigma_g^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.11 (0.2%) |
| $8\sigma_u^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.02 (0.0%) | 0.00 (0.0%) | 0.18 (0.4%) |
| $9\sigma_g^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.07 (0.1%) | 0.01 (0.0%) |
| $9\sigma_u^+$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.05 (0.1%) |
| Sum $\sigma$(HV) | 0.16 (0.4%) | 0.08 (0.1%) | 0.05 (0.1%) | 0.88 (1.7%) | 4.09 (8.1%) |
| $1\pi_u$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.01 (0.0%) |
| $1\pi_g$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.02 (0.0%) |
| $2\pi_u$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.02 (0.0%) |
| $2\pi_g$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.01 (0.0%) |
| $3\pi_u$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.01 (0.0%) |
| $3\pi_g$ | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.01 (0.0%) | 0.01 (0.0%) |
| Sum $\pi$(HV) | 0.00 (0.0%) | 0.00 (0.0%) | 0.00 (0.0%) | 0.05 (0.1%) | 0.08 (0.2%) |
| Total $\alpha_{zz}$ | 36.54 | 55.78 | 55.80 | 50.27 | 50.39 |

## S.VI. SUPPLEMENTARY FIGURES

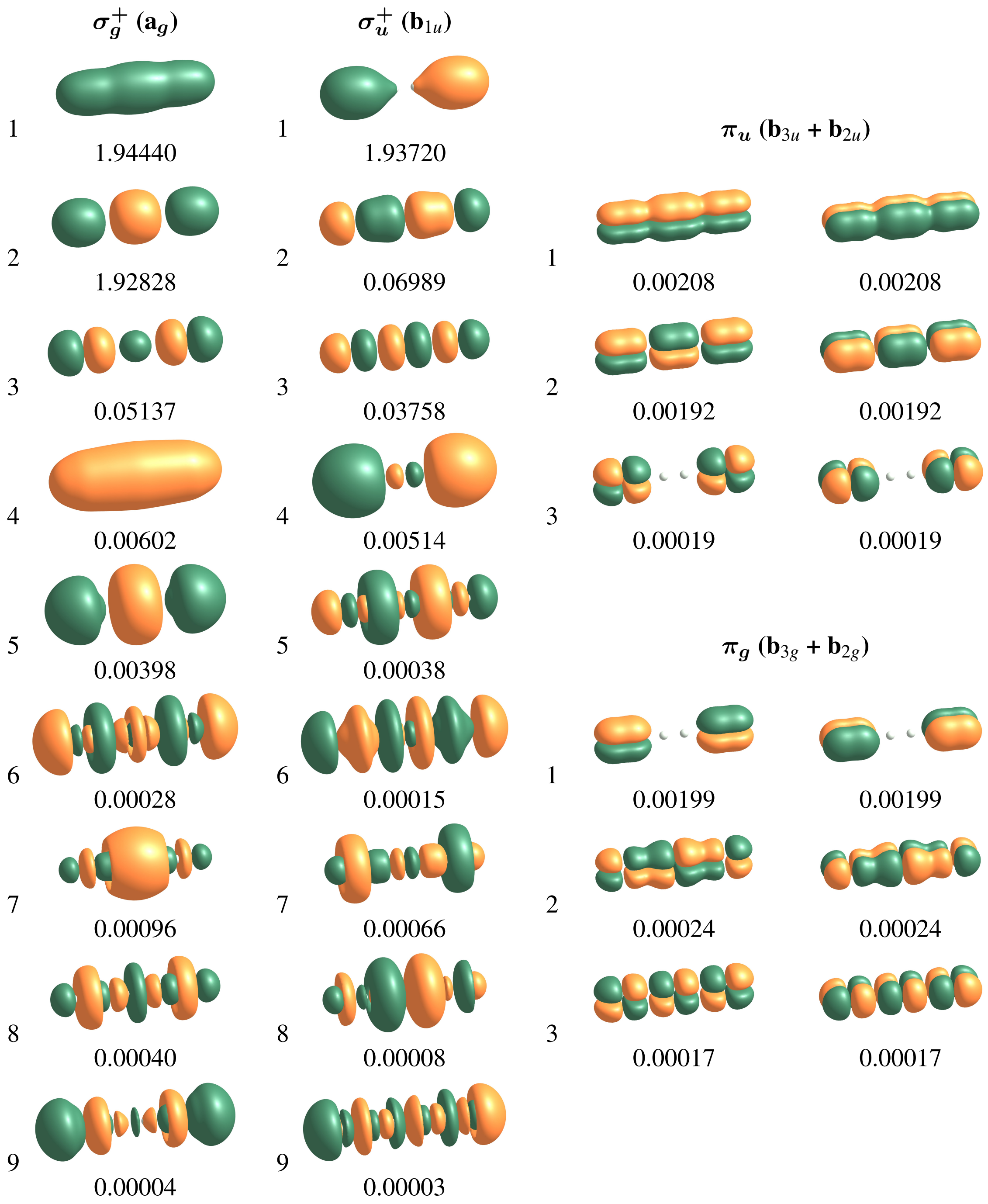

FIG. S.1. Cartesian representation of the NOs of the unperturbed ground state of $(H_2)_3$, obtained at the FCI/cc-pVDZ level of theory. The occupancy of each NO is presented below each orbital.

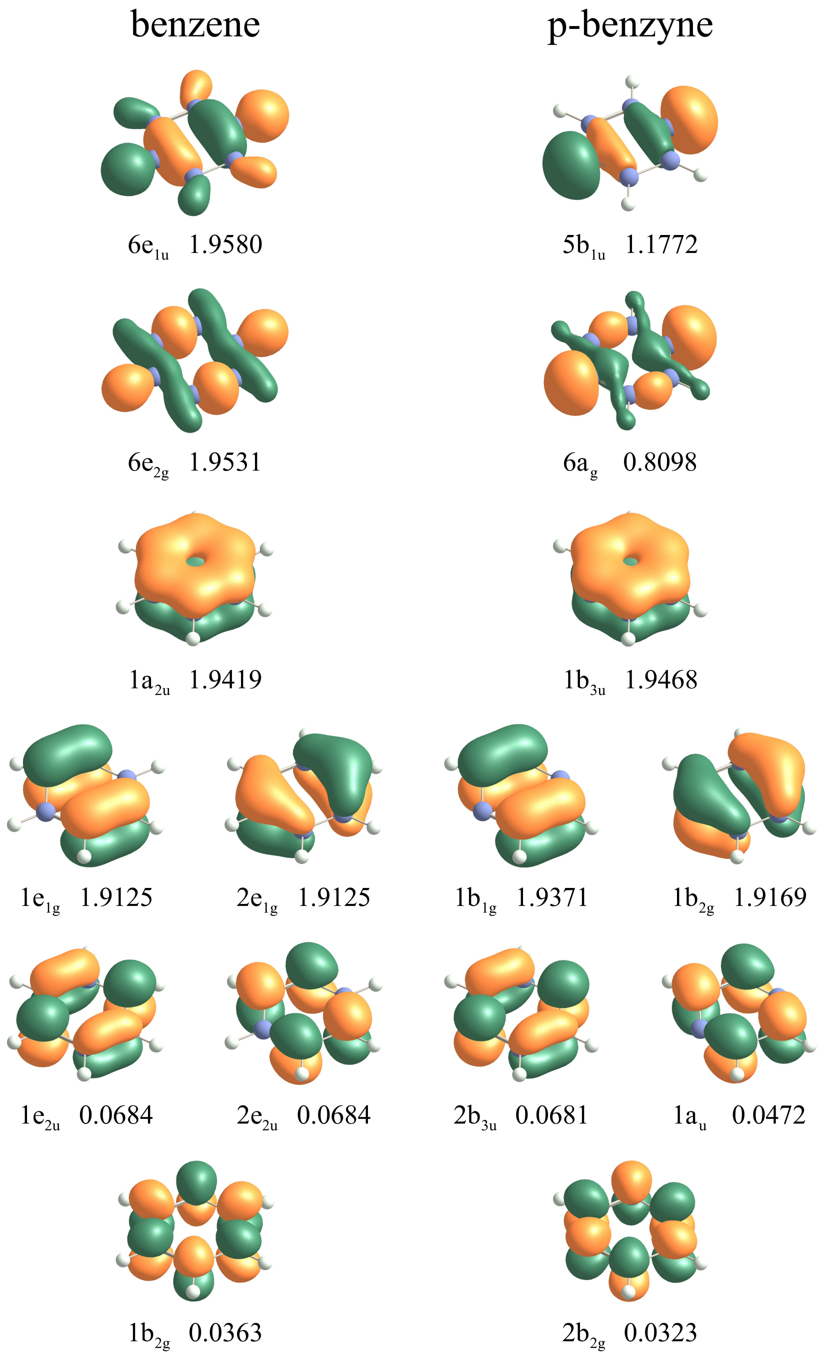

FIG. S.2. Graphical representation of selected NOs of benzene (left) and *p*–benzyne (right), along with their occupancies. Obtained at (U)CCSD/aug–cc–pVDZ level of theory.

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