# Analysis of Optical Activity in Terms of Bonds and Lone-Pairs: The Exceptionally Large Optical Rotation of Norborneneone[1]

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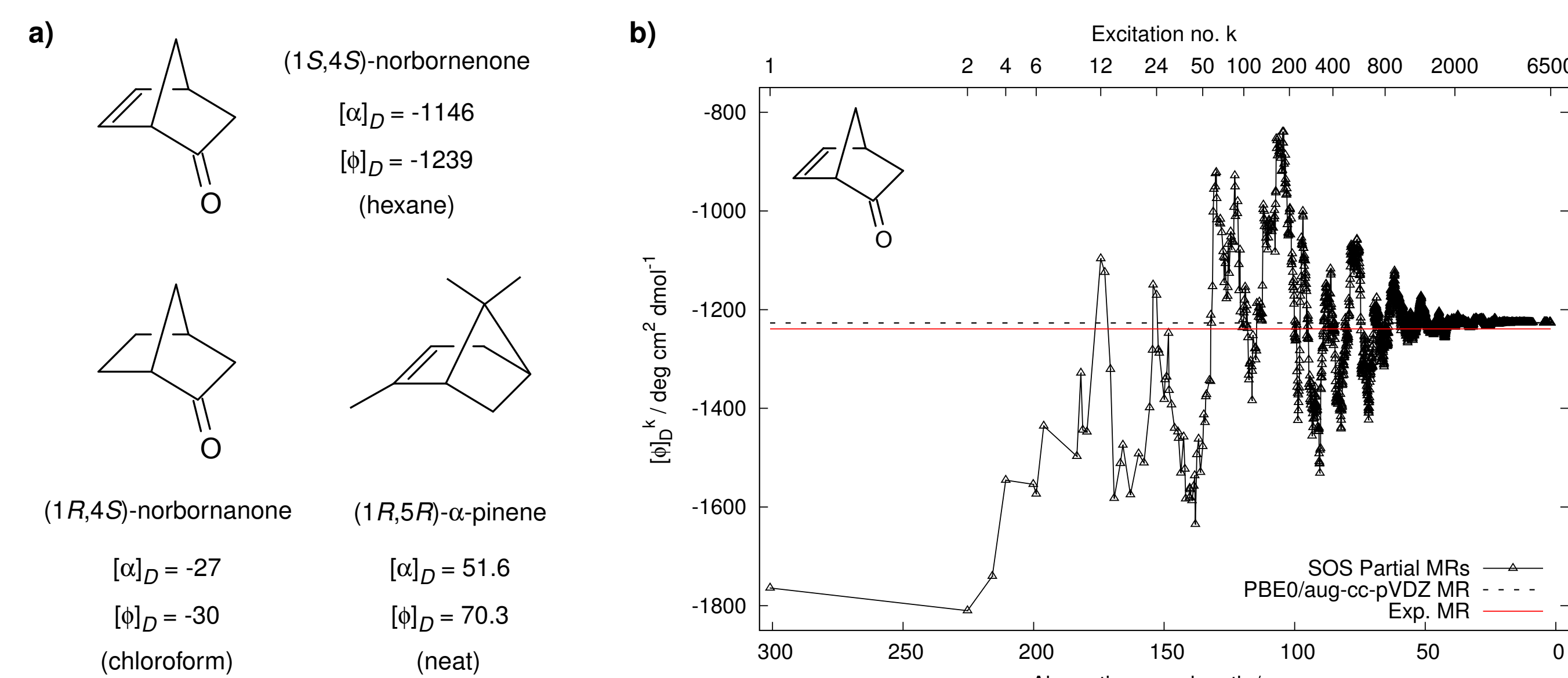
## Introduction



FIGURE 1: a) Some bicyclic organic molecules, and measured specific and molar optical rotations (in usual units) for $\lambda = 589.3$ nm. b) SOS molar optical rotation of norbornenone (PBE0/aug-cc-pVDZ). Experimental solution-phase OR and the result from a direct calculation of the OR.

## Functional Tuning

We use the following 3-parameter expression for the inverse interelectronic distance in the exchange functional:[2]

$$\frac{1}{r_{12}} = \frac{\alpha + \beta \, \text{erf}(\gamma r_{12})}{r_{12}} + \frac{1 - [\alpha + \beta \, \text{erf}(\gamma r_{12})]}{r_{12}} \quad (1)$$

where the first term on the right-hand side is used for the long-range HF part. In Equation (1), $\gamma$ is the range-separation parameter, $\alpha$ is the HF fraction at very small interelectronic distances, and $\alpha + \beta$ quantifies the fraction of HF exchange in the asymptotic limit at large interelectronic separations. A global hybrid such as B3LYP corresponds to $\beta = 0$, with $\alpha$ being the HF fraction of exchange in the functional.

We consider a range-separated hybrid variant of the PBE functional which satisfies the correct asymptotic behavior of the XC potential. It follows that $\alpha + \beta = 1$. Further, the functional is tuned to satisfy $-\varepsilon^{\text{HOMO}}(N) = \text{IP}(N)$ subject to the $\alpha + \beta = 1$ constraint. Following Reference 3, we minimize

$$J^2 = \sum_{i=0}^{1} [\varepsilon^{\text{HOMO}}(N+i) + \text{IP}(N+i)]^2 \quad (2)$$

to satisfy the IP condition simultaneously for the system with $N$ and $N + 1$ electrons, where $\text{IP}(N) = E(N) - E(N-1)$ is calculated as a difference of total energies. This optimization is performed in the $\alpha = 1 - \beta$ vs. $\gamma$ plane, which is the reason why the procedure is referred to as a 'two-dimensional' tuning here. The tuning was accomplished as follows. Hartree-Fock molecular orbitals were calculated for the neutral ($N$ electrons), anion ($N + 1$), and cation ($N - 1$) systems. These molecular orbital vectors were then used as initial guesses for DFT calculations with the PBE0 global hybrid functional. The PBE0 molecular orbital vectors were used as input for calculations with $\alpha$ between 0 and 0.5 and $\gamma$ between 0 and 0.5 on the tuning grid. MOs from calculations with $\alpha = 0.5$ and a given $\gamma$ were used as initial guesses for calculations with $\alpha$ ranging from 0.6 to 0.8 and the same value of $\gamma$ in order to improve convergence of the self-consistent field (SCF) procedure. Finally, for sets $\{\alpha, \beta = 1 - \alpha, \gamma\}$ satisfying the IP condition, we investigate the DFT delocalization error, quantified by the curvature of $E(N)$.
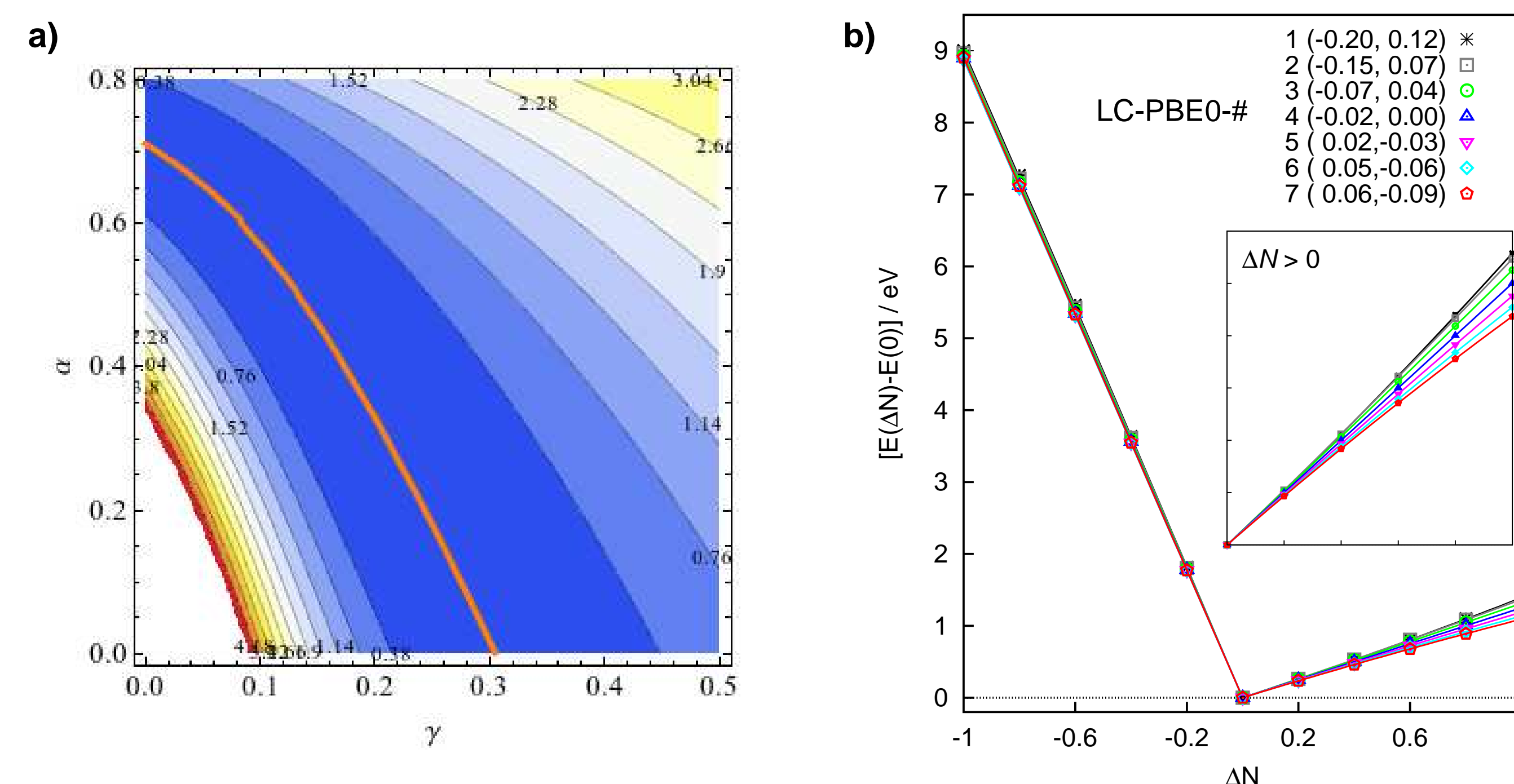
## a)



## b)

FIGURE 2: a) Contour plot of $J^2$ as a function of $\alpha$ and $\gamma$. The thick orange line corresponds to $J^2 \approx 0$. b) Energy of norbornenone as a function of fractional electron number, $\Delta N$, relative to neutral system ($\Delta N = 0$) for tuned LC-PBE0-# parameterizations. The numerical values in parentheses correspond to $(\Delta N)^2$ coefficients of quadratic fits to $E(N)$ in the electron-deficient and electron-rich regime, respectively ($\Delta N < 0$, $\Delta N > 0$). The inset shows the $E(N)$ behavior in the electron-rich regime.
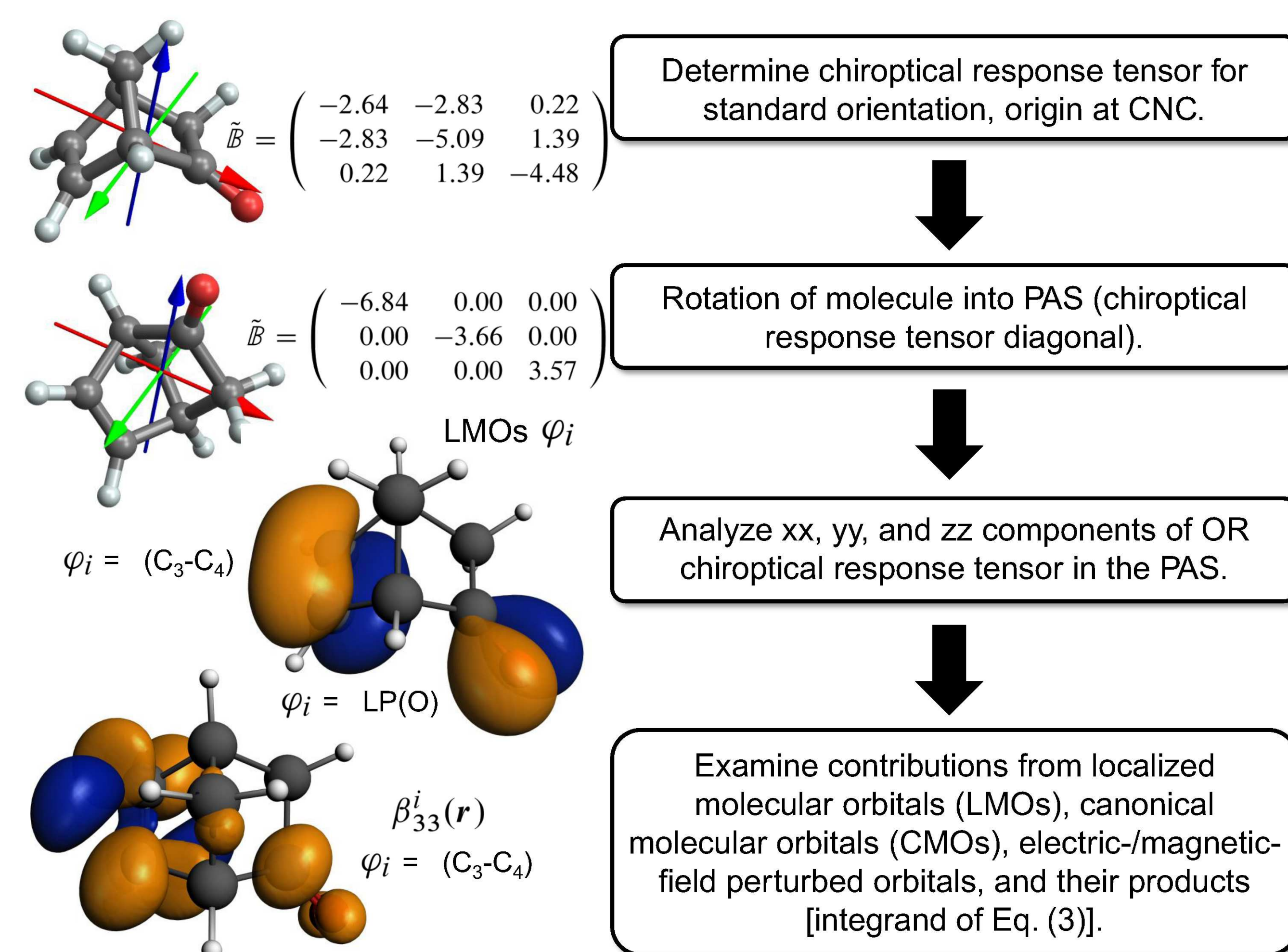
## Analysis Protocol



FIGURE 3: Flowchart for OR analysis. CNC = center of nuclear charges, PAS = principal axis system of $\tilde{\mathbb{B}}$.

$$\beta(\omega) = -\frac{2}{3} \text{Im} \sum_{u=x,y,z} \sum_{i} \left\langle \frac{\partial \varphi_i}{\partial E_u(+\omega)} + \frac{\partial \varphi_i}{\partial E_u(-\omega)} \left| \frac{\partial \varphi_i}{\partial B_u(0)} \right\rangle \right. := \frac{1}{3} \sum_{u=x,y,z} \sum_{i} \int \beta_{uu}^i(\mathbf{r}) dV \quad (3)$$
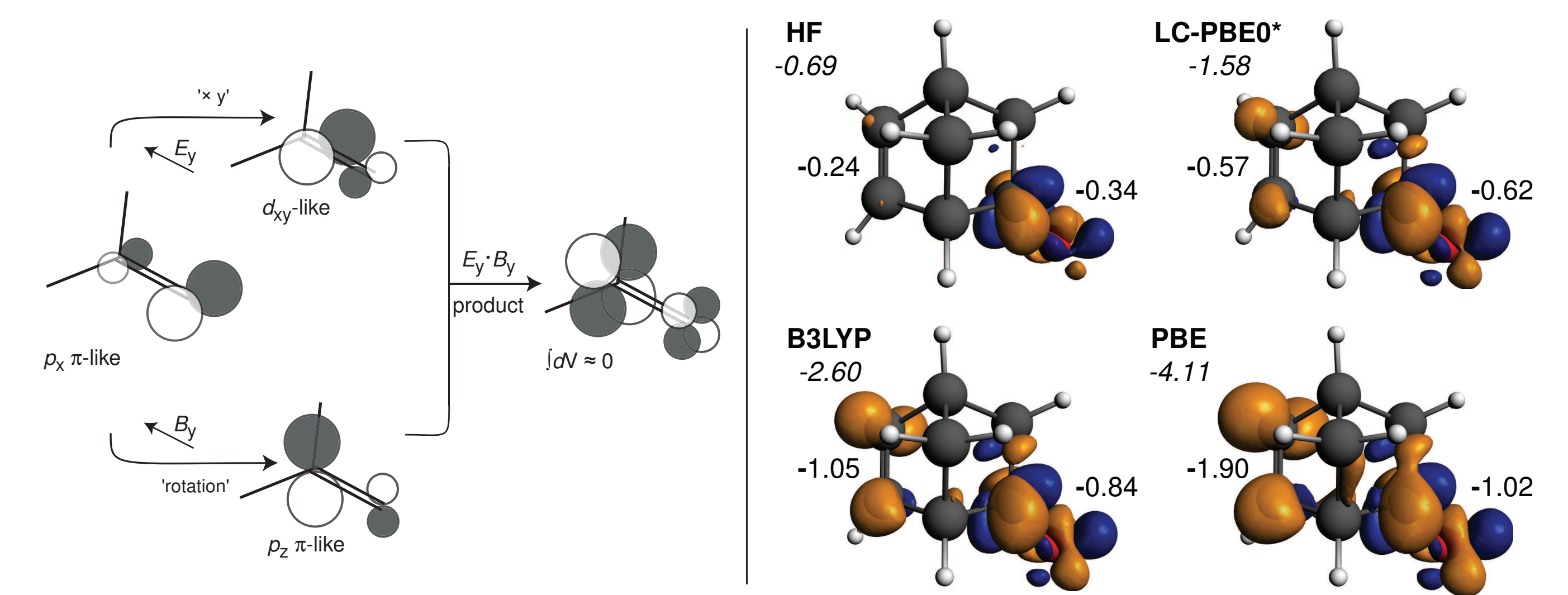
## Results and Discussion



FIGURE 4: Left: Qualitative interpretation of the electric- and magnetic-field perturbations of the $\pi$LP(O) orbital at the carbonyl group via construction of the integrand of Eq. (3). Right: Static $\beta_{33}^i(\mathbf{r})$ for $i = \pi$LP(O) (isosurfaces 0.028 au). The numbers listed are the total orbital contributions to $\beta_{33}$ obtained upon volume integration (italic), and approximate numerical integrations within low-value isosurfaces centered at the C=C and C=O moieties, respectively.
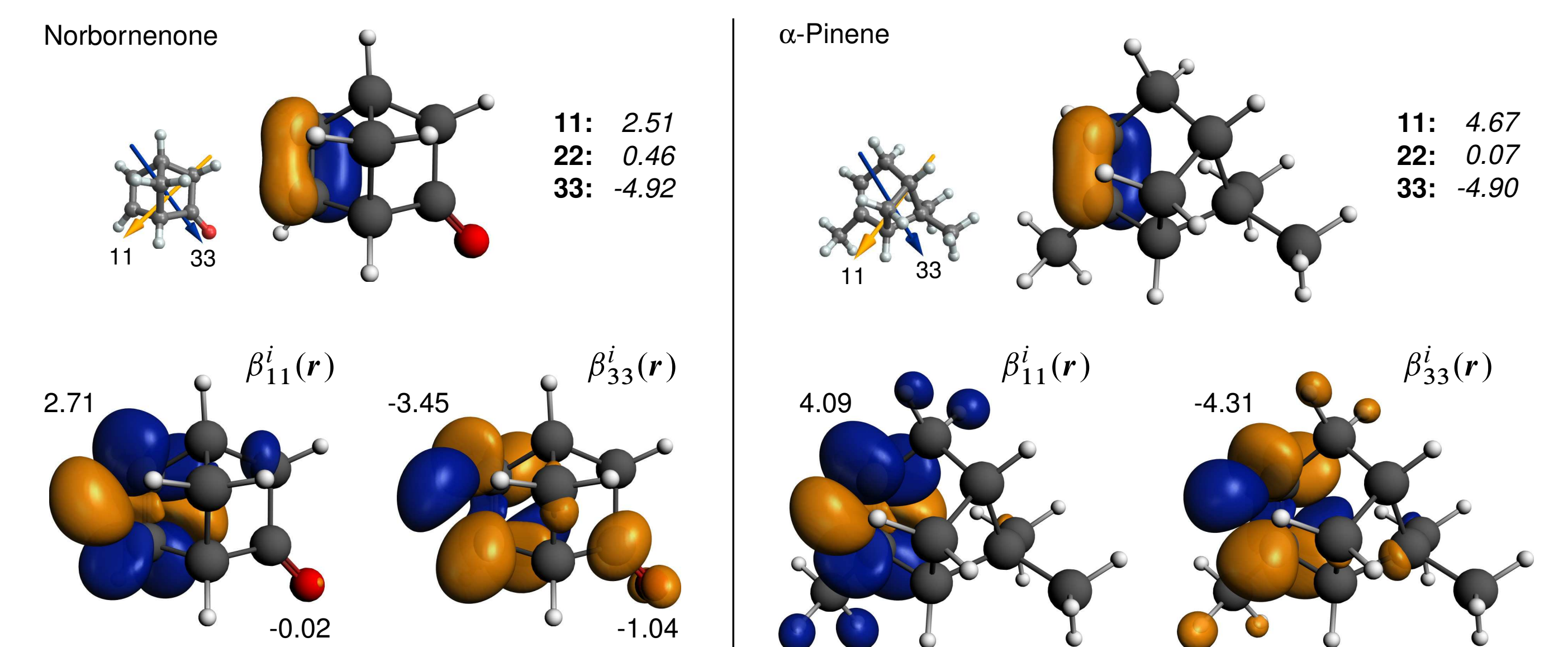


FIGURE 5: Top: Isosurfaces of the $\pi$(C=C) LMO (0.1 au), and their contributions to $\beta$ tensor for norbornenone and $\alpha$-pinene. Bottom: Isosurfaces (0.04 au) of $\beta_{11}^i(\mathbf{r})$ and $\beta_{33}^i(\mathbf{r})$ for $\pi$(C=C), and approximate numerical integrations within isosurfaces centered at the C=C and C=O moieties, respectively. LC-PBE0* functional.

## Acknowledgements

## References

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