

Abstract

Norbornenone, which has both a C=O and a C=C chromophore in a rigid bicyclic hydrocarbon framework, exhibits optical rotation (OR) an order of magnitude larger than that of similar molecules with only one of these chromophores (e.g., α -pinene). Its OR is also very sensitive to approximations in electronic structure calculations. The present study demonstrates a novel approach to interpret optical rotation using familiar concepts of chemical bonding, aided by first-principles calculations. A theoretical procedure is developed for analyzing the OR tensor components of a molecule in terms of individual bonds and lone pairs. The link between the chemists bond and quantum mechanics is provided by localized molecular orbitals obtained from density functional theory (DFT) calculations. Delocalization of π orbitals is shown to play a crucial role in the large OR of norbornenone, as hinted by the DFT delocalization error inherent in many standard functionals and confirmed by detailed analysis. The OR contributions generated by the double bond in α -pinene are even stronger than that of norbornenone. The isotropic average, observed in solution or in gas phase, is small as a result of cancellation of tensor components with opposite signs. The electronic coupling and delocalization of the C=C π bond and the C=O oxygen π lone pair in norbornenone selectively enhance one of the OR tensor components, resulting in the exceptionally large negative isotropic OR.

Functional Tuning

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

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

where the first term on the right-hand side is used for the long-range HF part. In Equation (1), γ is the range-separation parameter, α 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 α 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. γ 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 α between 0 and 0.5 and γ between 0 and 0.5 on the tuning grid. MOs from calculations with $\alpha = 0.5$ and a given γ were used as initial guesses for calculations with α ranging from 0.6 to 0.8 and the same value of γ 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 $E(N)$.

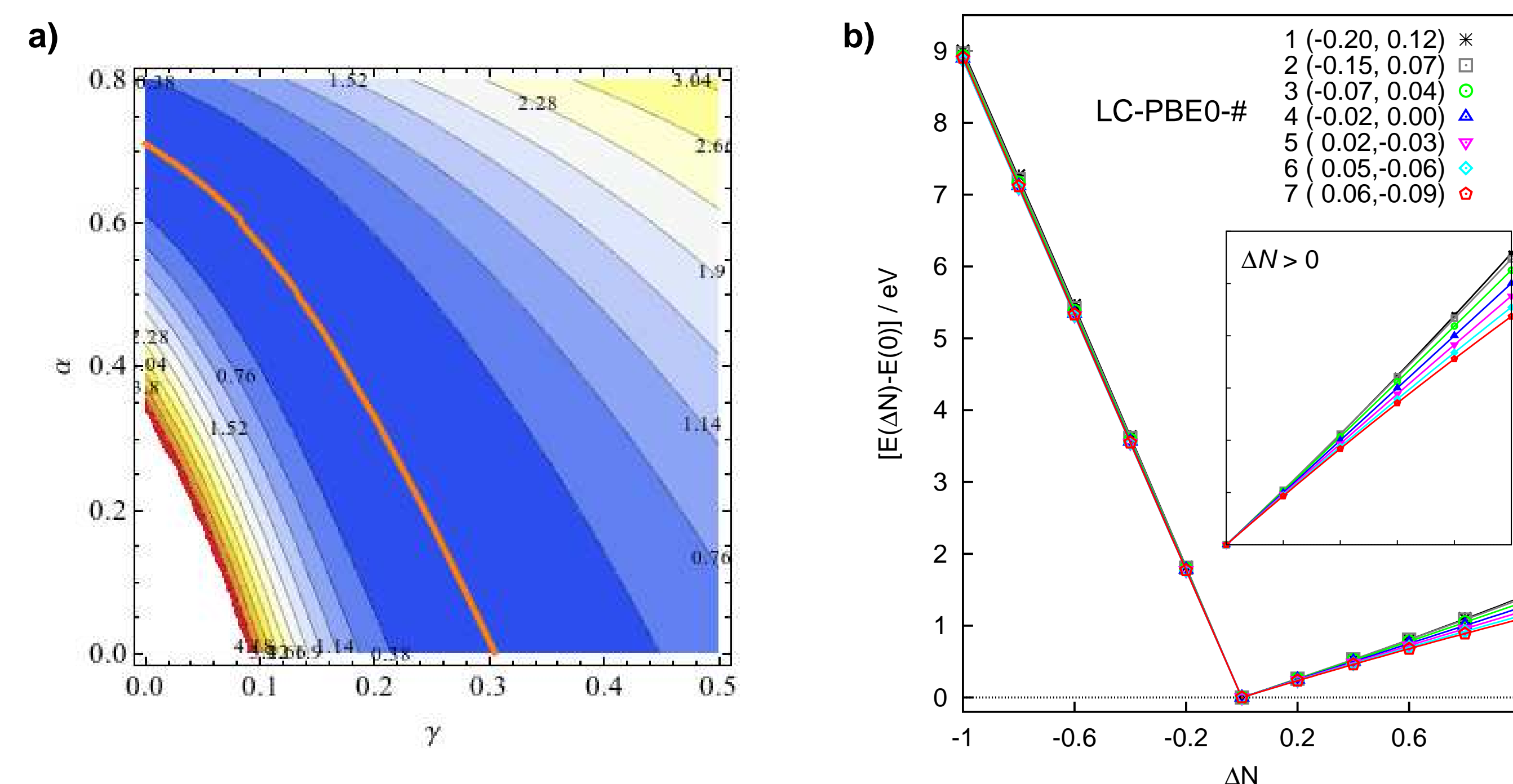


FIGURE 1: a) Contour plot of J^2 as a function of α and γ . The thick orange line corresponds to $J^2 \approx 0$. b) Energy of norbornenone as a function of fractional electron number, ΔN , relative to neutral system ($\Delta N = 0$) for tuned LC-PBE0-# parameterizations. The numerical values in parentheses 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

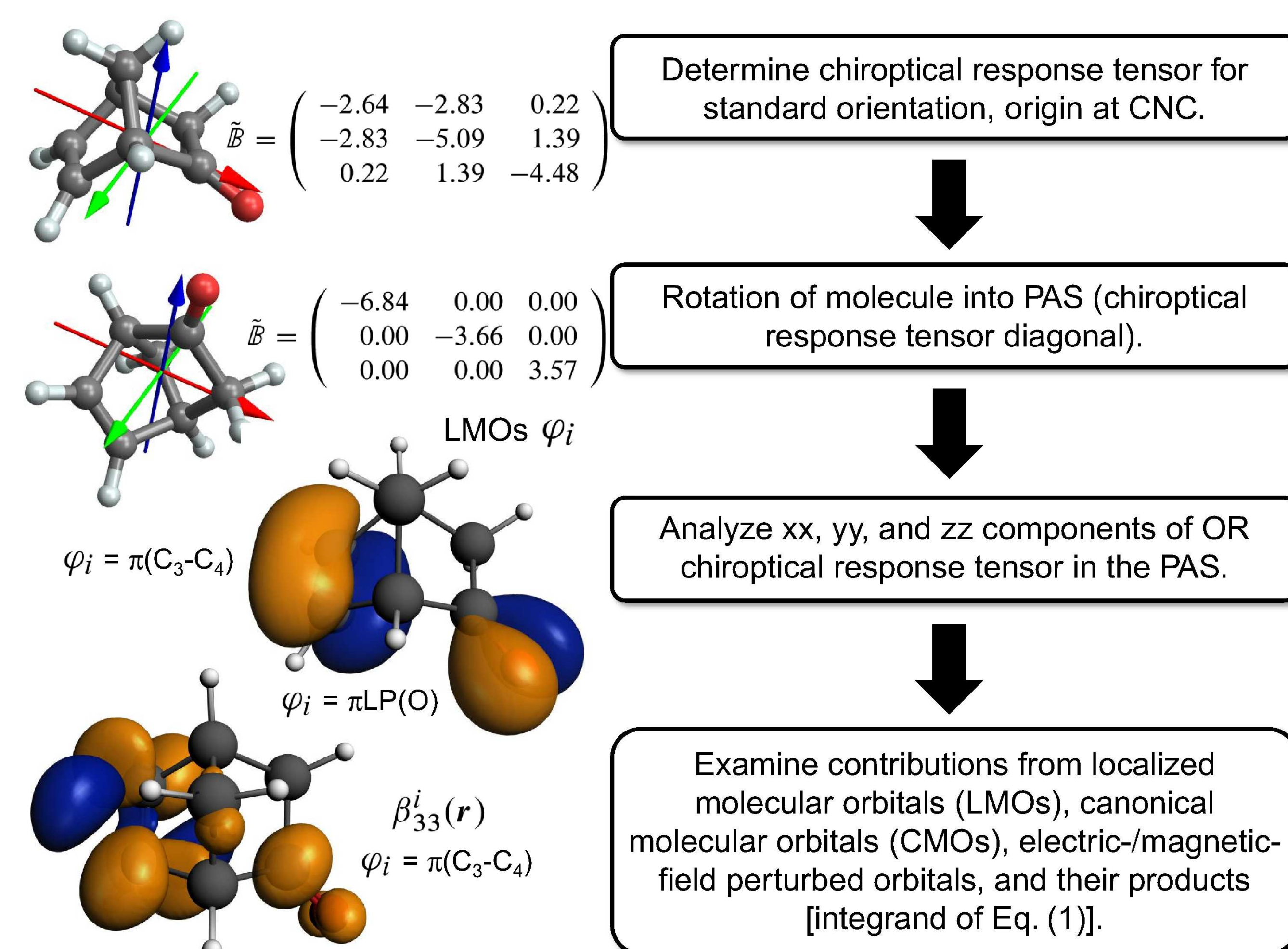


FIGURE 2: Flowchart for OR analysis. CNC = center of nuclear charges, PAS = principal axis system of $\tilde{\mathbb{B}}$.

Results and Discussion

Electron delocalization plays a paramount role in the optical rotation (OR) of norbornenone. This conclusion is evident from an analysis in terms of individual ‘chemist’s orbitals’ (localized MOs). Delocalization of the C=C π bond over the C=O group, and delocalization of the carbonyl oxygen π lone-pair orbital over the C=C moiety, result in a significantly enhanced component of the OR tensor in the direction of the C=O bond, β_{33} . Contributions from the bridging C-C σ bonds are also very important, as one might expect if delocalization between the C=C and C=O π orbitals is significant. The strong enhancement of the negative β_{33} is not balanced by other tensor components which results in a large negative isotropic optical rotation of norbornenone. A comparison with α -pinene, which has a more localized C=C π bond as a composition of the corresponding ‘natural LMO’ revealed (magnitudes below < 0.4 on adjacent and distant carbons clearly shows how geometry and electronic structure effects in norbornenone all cooperate to yield an enhancement of β_{33} .

It is clear that one can dig much deeper in an attempt to fully rationalize the magnitudes and the signs of all orbital contributions to the optical activity of norbornenone, α -pinene and countless other molecules. The present work is intended to provide an initial assessment of the analysis technique and to address long standing problems with OR calculations for norbornenone. Further, we hope to have demonstrated that with suitable theoretical tools it is possible to gain an in-depth understanding of optical rotation. We expect to be able to provide additional examples in subsequent publications and, in particular, consider the optical rotation created by chiral σ -frameworks.

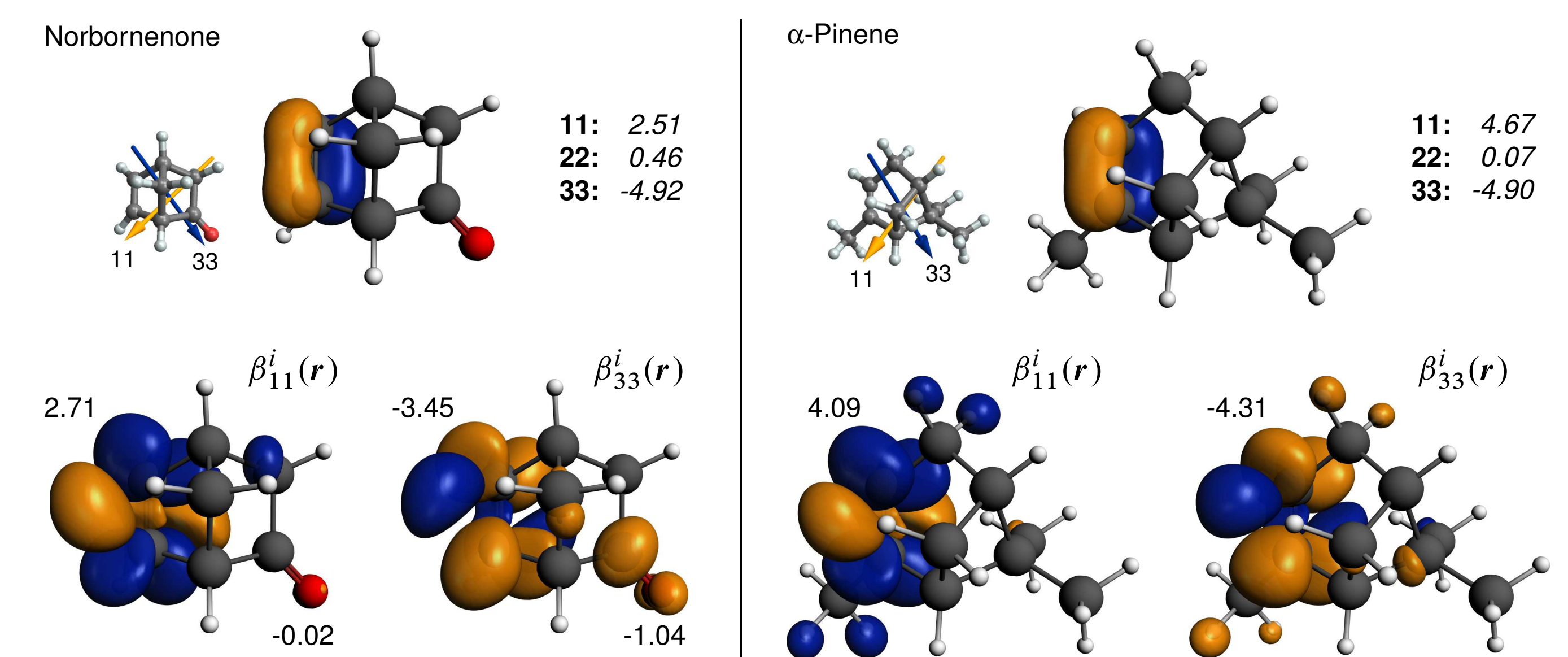


FIGURE 3: Static chiroptical response tensor $\tilde{\mathbb{B}}$ for norbornenone and α -pinene, and principal components. Yellow and blue indicate negative and positive optical rotation for a given direction. Surfaces were scaled to 30 pm per atomic unit. LC-PBE0* functional. Values in parentheses are diagonal components of β .

Acknowledgements

This research has been supported by the National Science Foundation, Grant No. CHE 0952253 to J.A. M.S. is grateful for financial support from the Foundation for Polish Science (START scholarship) as well as from the Polish Ministry of Science and Higher Education (Mobility Plus program). We thank the Center for Computational Research at the University at Buffalo for supporting our research.

References

- [1] Moore, B.; Srebro, M.; Autschbach, J. *J. Chem. Theory Comput.* **2012**, *8*, 4336-4346.
- [2] Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51-57.
- [3] Kuritz, N.; Stein, T.; Baer, R.; Kronik, L. *J. Chem. Theory Comput.* **2011**, *7*, 2408-2415.