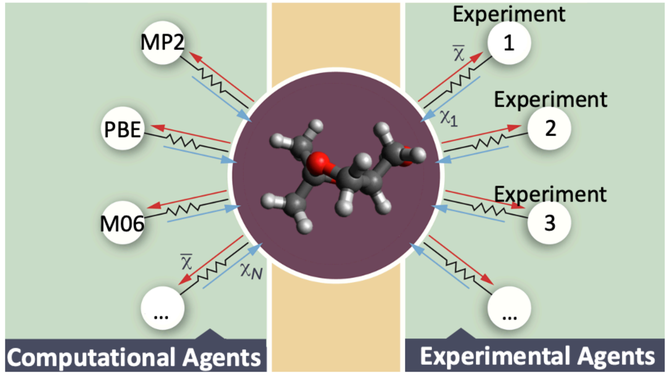
# Consensus Equilibrium in Electronic Structure Determination

Jiayue Rong, Lyudmila Slipchenko, Charlie Bouman, Greg Buzzard and Garth J. Simpson*

*Department. of Chemistry, Purdue University, West Lafayette, IN 47907, USA*

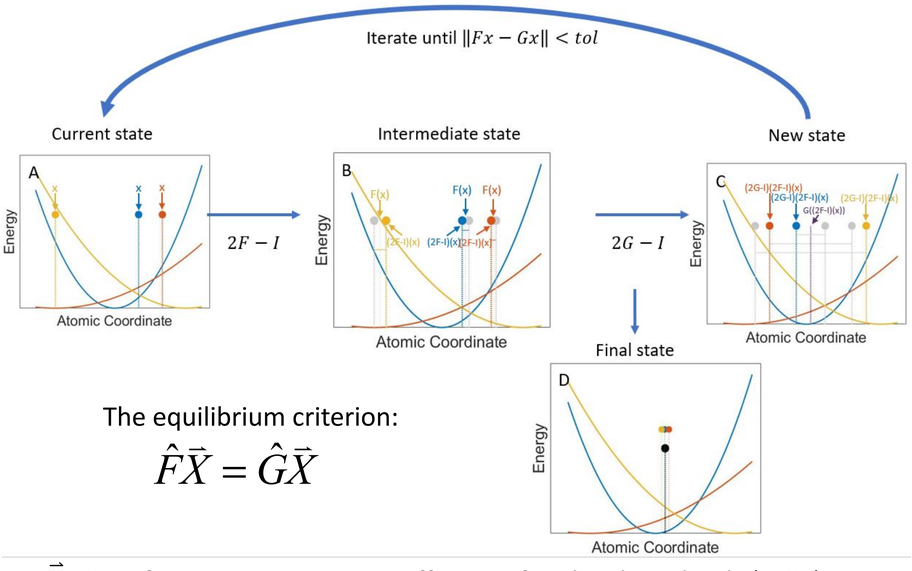
** gsimpson@purdue.edu*

## The Need for Data and Theory Fusion




Investigations into the physical nature of complex phenomena increasingly depend upon the unified investigation of theoretical and experimental methods. However, as the size and complexity of these systems increases, quantum chemical simulation methods become increasingly costly, particularly in studies pertaining to extended solid state systems and large protein complexes. Consequently, methods which enhance numerical accuracy while minimizing the corresponding computational scaling with respect to system size are highly desirable. Multi-agent consensus equilibrium is a criterion which may be used with convex sets of functions to fuse multiple sets of data, under the constraint that each agent describes the system in the same dimensionality.

## MACE to Fuse Multiple Models




The equilibrium criterion:

$$\hat{F}\vec{X} = \hat{G}\vec{X}$$

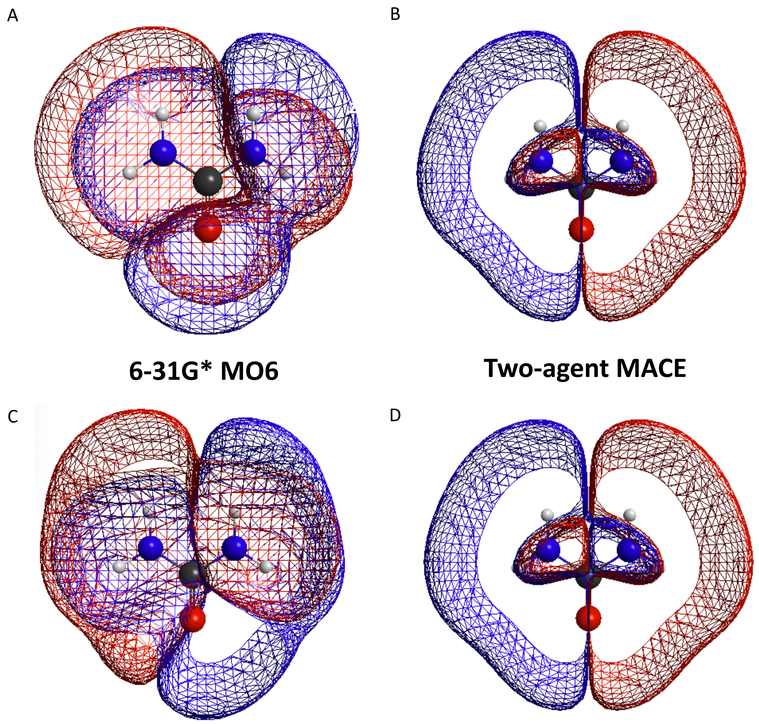
$\vec{X}$: Set of state vectors, e.g., coefficient of molecular orbitals (MOs)

$\hat{F}$ : Agent operator; takes a single step for each agent

$\hat{G}$: Broadcast mean operator; anchors the agents together

(A) Current state; each model begins in a different state, with each color representing a different potential produced by a computational agent. B) Intermediate state; Grey balls represent states before 2F-I operation, and colored balls represent states after 2F-I operation. application of the 2F-I operation for each agent (potential) advances the atomic position along the potential to F(x), then reflects the current state x about F(x) to (2F-I)(x). C) New state; Grey balls represent states before 2G-I operation, and colored balls represent states after 2G-I operation. the mean of the (2F I)(x) positions is calculated as G(2F-I)(x), and the updated positions are evaluated by reflection about that location for each agent as (2G-I)(2F I)(x). D)Final state; When the difference of F(x) (showed in colored ball) and G(x) showed in black ball is smaller than tolerance, the consensus equilibrium conditions is met and the calculation completed.

## Evaluation of MACE on Computational Models

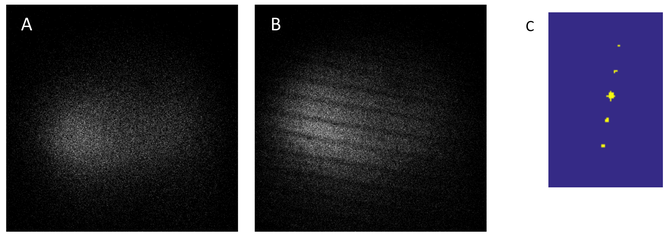



**6-31G* MO6** | **Two-agent MACE**

**6-31G* PBE** | **Averaged 6-31G* PBE and MO6**

isotherphase plot LUMO gap. (A) and (C) are 6-31G* PBE and 6-31G* MO6. (B) two-agent MACE fusion of 6-31G* PBE and 6-31G* MO6. (C) averaged 6-31G* PBE and MO6. Apparently averaged result is different from MACE fusion the MACE result is not equivalent to averaging the optimum structure for each agent individually

## Go beyond Theory – Adding Circular Dichroism measurements as Experimental Constraint




| FOV | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| -CLD | .3593 | .3579 | .3569 | .3743 | .3777 | .3715 | .3806 |

(A) Epi-two photon excited UV fluorescence (TPEUVF) image of tryptophan solution on FOV 1 (B) Image of (A) with a micro-retarder array (μRA) placed in the rear conjugate plane of SONICC (C) FFT analysis on difference between (A) and (B). Five peaks are harmonics. Table: CLD on uniform tryptophan solution on different FOV. Avg = -0.3539, STD = 0.0072

## Foundation of TPA-CLD integration in MACE

$$R \cong \frac{\cos^2\theta + 3}{2(2\cos^2\theta + 1)}, where\ \cos\theta = \frac{\vec{\mu}^T \cdot \vec{\delta}}{|\vec{\mu}| \cdot |\vec{\delta}|} = \vec{\mu}^T \cdot \hat{\delta}$$

$$\begin{aligned} \text{cost function } \nabla U &= \nabla \|R_{\text{calculation}} - R_{\text{measurement}}\|^2 \\ &= \nabla\left[R_{\text{calc}}^2 - 2R_{\text{mea}}R_{\text{calc}} + R_{\text{mea}}^2\right] \\ &= \nabla\left[R_{\text{calc}}^2 - 2R_{\text{mea}}R_{\text{calc}}\right] \\ &= \nabla R_{\text{calc}}\left[R_{\text{calc}}COMPUTATI - 2R_{\text{mea}}\right] \end{aligned}$$

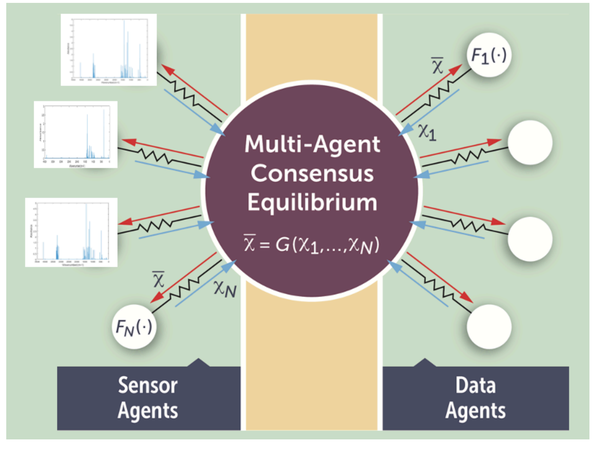
$$\nabla R_{\text{calc}} \cong \frac{\cos^2\theta + 3}{2(2\cos^2\theta + 1)}, where\ \cos\theta = \frac{\vec{\mu}^T \cdot \vec{\delta}}{|\vec{\mu}| \cdot |\vec{\delta}|} = \vec{\mu}^T \cdot \hat{\delta}$$

$$\nabla R_{\text{calc}} \cong \frac{1}{4}\left(\frac{5}{2\cos^2\theta + 1} + 1\right) = \frac{5}{4}\left(\frac{1}{2\cos^2\theta + 1}\right) + \frac{1}{4}$$

Above is the gradient evaluation in MACE with two-photon absorption (2PA) circular–linear dichroism (CLD) spectroscopy measurement derived TPA-CLD ratio as an experimental agent.

## Further Steps

- Integration and visualization of 2PA-CLD spectroscopy into MACE for electronic structures of small model molecules and amino acids
- Expand to label-free protein measurement (e.g., lysozyme)
- Apply MACE into Vibrational spectroscopy




## References

I. Ulcickas, J. R. W.; Cao, Z.; Rong, J.; Bouman, C. A.; Slipchenko, L. V.; Buzzard, G. T.; Simpson, G. J. Multiagent Consensus Equilibrium in Molecular Structure Determination. J. Phys. Chem. A 124 (43), 9105–9112, 2020.

## Acknowledgement

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