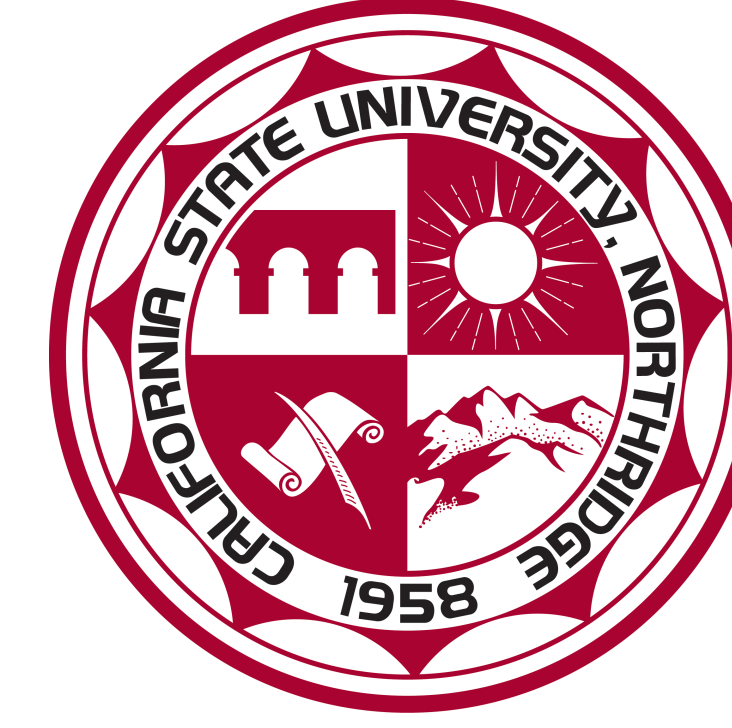


# Applications of Imaginary Time Propagation Method in Material Research

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## the Imaginary Time Propagation

The imaginary time propagation method (ITP) relies on solving the time-dependent Schrödinger equation in imaginary time. We perform a Wick Rotation (setting  $t = -i\tau$ ) to transform the time-dependent Schrödinger equation into a simple diffusion equation

$$\frac{\partial \psi(r, \tau)}{\partial \tau} = -\frac{\hat{H}}{\hbar} \psi(r, \tau) \implies \psi(r, \tau) = \exp(-\hat{H}\tau/\hbar) \psi(r, 0) \quad (1)$$

**Iterative Solutions to Eigenproblems** This can be thought of as the analog to a power solution or subspace iteration. As  $\tau \rightarrow \infty$ ,  $\psi(r, \tau)$  will converge on the eigenfunction for the ground state.

In order to implement the solution computationally, the exponential operator is approximated using the Cayley unitary form, transforming the eigenvalue problem into a linear problem:

$$\exp(-H\Delta\tau) \approx \left(1 + \frac{1}{2}H\Delta\tau\right)^{-1} \left(1 - \frac{1}{2}H\Delta\tau\right) \implies \left(1 + \frac{1}{2}H\Delta\tau\right) \psi(r, \tau + \Delta\tau) = \left(1 - \frac{1}{2}H\Delta\tau\right) \psi(r, \tau) \quad (2)$$

**Stopping Criteria** A formula for the absolute error,  $\Delta E_i$  present in  $E_i(\tau)$  can be written in terms of the quantum mechanical standard deviation of  $H$  and is used as a stopping criteria.

$$\Delta E_i = |E_i - \langle \psi_i(r, \tau) | H | \psi_i(r, \tau) \rangle| \leq \sqrt{2} \sqrt{\langle \psi_i(r, \tau) | H^2 | \psi_i(r, \tau) \rangle - \langle \psi_i(r, \tau) | H | \psi_i(r, \tau) \rangle^2} \quad (3)$$

## Applications to Bosonic Density Functional Theory

Helium clusters were modeled by the Orsay-Trento DFT (OT-DFT) and the interaction with the guest molecule was included through an external potential. To compute the effective moment of inertia of the molecule-helium complex, we include an additional energy term of the form  $-\omega L_z$  and compute the “rotating” groundstate energy by minimizing

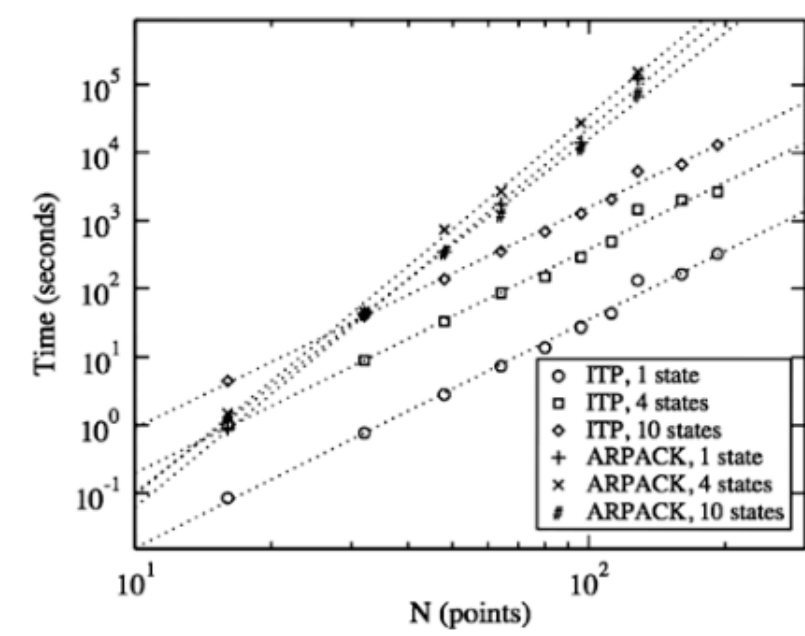
$$E[\Psi, \omega] = \int \left\{ \frac{\hbar^2}{2m} |\nabla \Psi|^2 + \epsilon_{OT}[\Psi] + V_{X-\text{He}} |\Psi|^2 - \omega \Psi^* L_z \Psi \right\} \quad (4)$$

The non-linear Schrödinger-type equation arising from the minimization of eq. 4 is solved by means of imaginary time propagation.

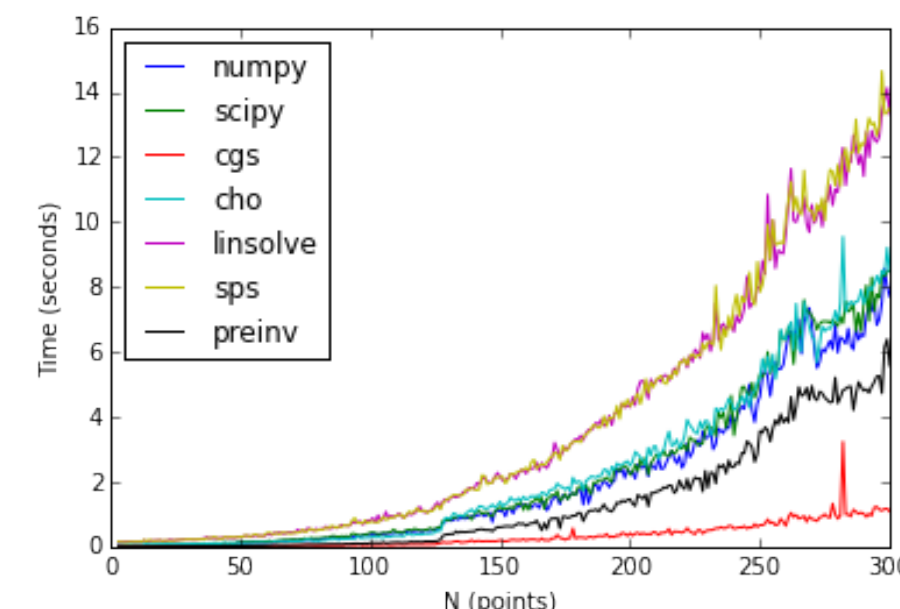
## Results

The ITP method reduces the solving of an eigenproblem to an iterative power solution via the solution of a linear equation. In current practice has been shown to have better scalability than the implicitly restarted Lanczos method as implemented in ARPACK.

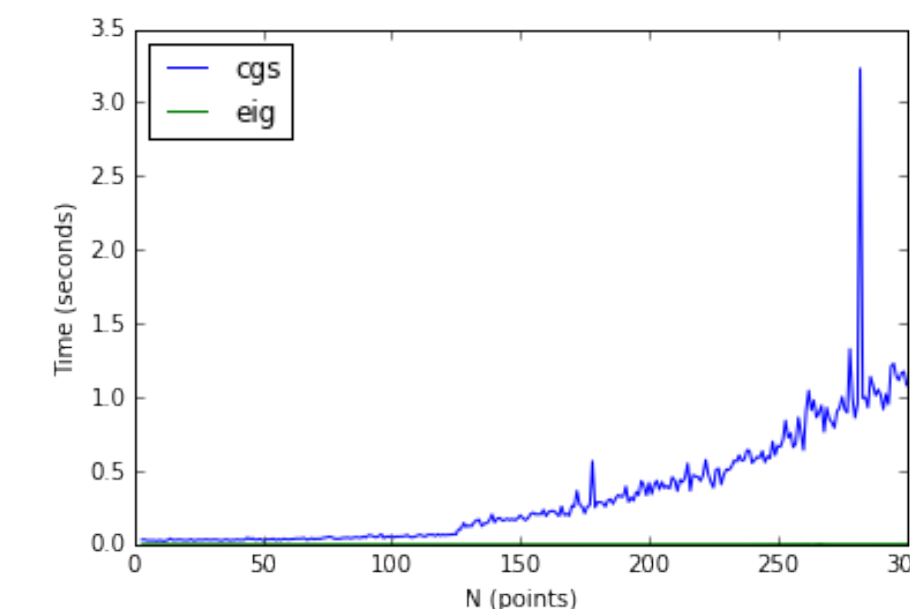
For the purposes of training, the algorithm is being reimplemented in Python and Numpy/Scipy. The solution of the linear equation being the most computationally expensive, theoretically involving a matrix inversion at each iteration, seven linear solution schemes were speed-tested versus Numpy’s built-in eigensolver: the Numpy solver, the Scipy solver, Scipy’s conjugate gradient squared (CGS) solver, a Cholevsky decomposition method, two of Scipy’s sparse solvers, and a pre-inversion of the matrix iterated.



**Figure 1:** Computational scaling of the ITP and implicitly restarted Lanczos methods (ARPACK) for 1, 4 and 10 states.



**Figure 2:** Implementation of seven linear solving schemes in Python.



**Figure 3:** Conjugate Gradient Squared Solver ITP v Built-in Eigensolver

The CGS solver was found to be the fastest. In comparison to the built-in eigensolver, however, it falls well short of reasonable performance standards. Furthermore, the CGS method has been found to be the least stable of the methods (note the spike at  $N \approx 280$ ).

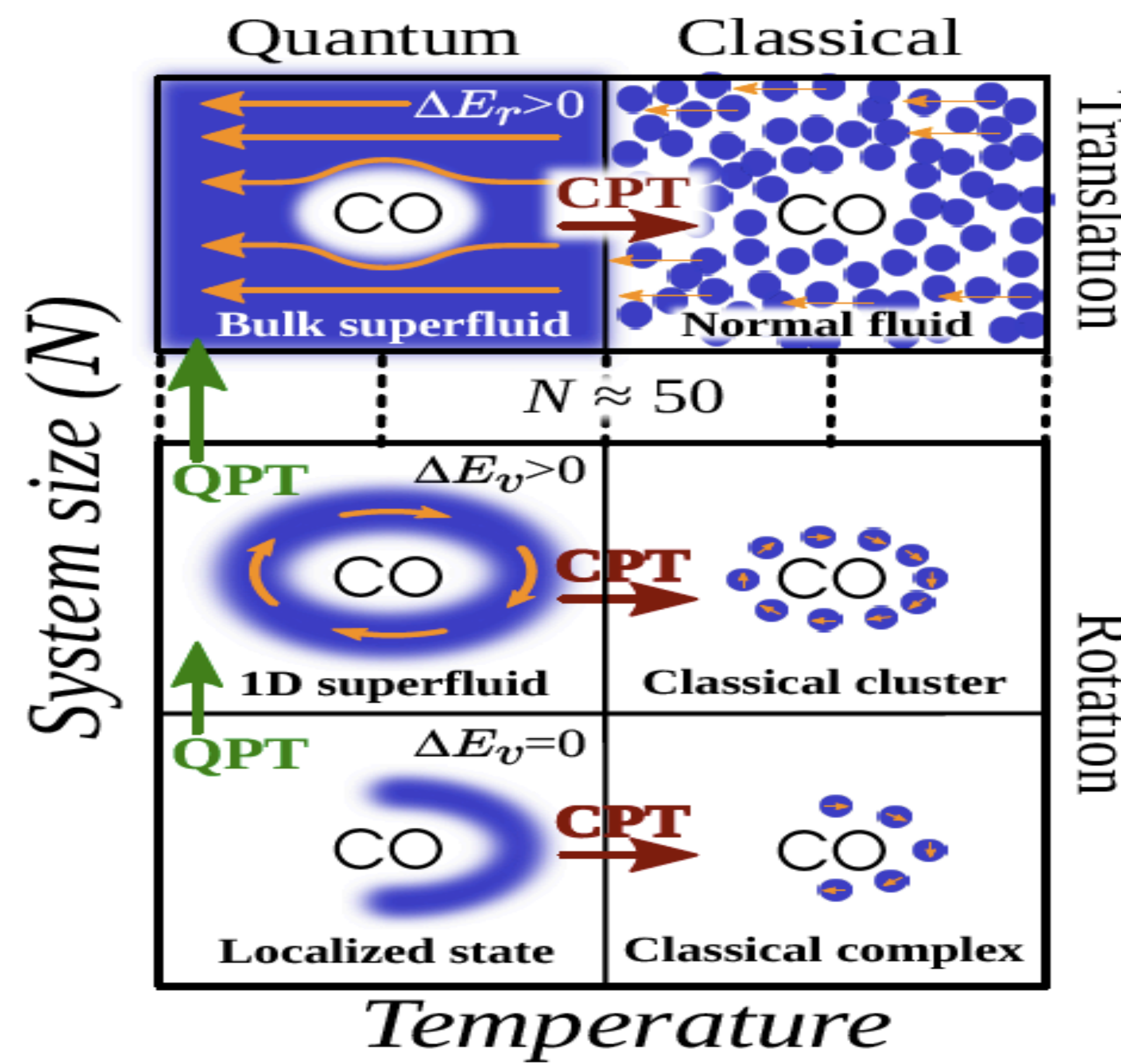
## Abstract

Helium droplets not only provide a unique matrix environment for high resolution spectroscopy and studying molecular solvation but also allow to use guest molecules as probes of the surrounding quantum medium.<sup>13</sup> After the initial discovery of the helium droplet technique for spectroscopic applications, attention quickly turned into characterizing the physical properties of the helium droplets themselves. The groundbreaking experiments by the Toennies group employed the glyoxal molecule as a probe to study the helium droplet response through optical absorption spectrum.

## Bosonic Density Functional Theory

In the experiment, bosonic density functional theory (DFT) is the method used to obtain calculated rotational constant values. Density functional theory is a technique that plays an important role in determining the key components that can explain why the moment of inertia decreases when rotational superfluidity takes place. The results obtained using DFT are compared with experimental data and Quantum Monte Carlo (QMC) values and there is a similar agreement which is shown by the appearance first-turn over point.

The first minimum appearing in molecular rotational constants as a function of helium droplet size has been previously associated with the onset of superfluidity in these finite systems. We investigate this relationship by bosonic density functional theory calculations of classical molecular rotors (OCS, N<sub>2</sub>O, CO and HCN) interacting with the surrounding helium. The calculated rotational constants are in fair agreement with the existing experimental data, demonstrating the applicability of the theoretical model. By inspecting the spatial evolution of the global phase and density, the increase in the rotational constant after the first minimum is shown to correlate with continuous coverage of the molecule by helium and appearance of angular phase coherence rather than completion of the first solvent shell. We assign the observed phenomenon to quantum phase transition between a localized state and one-dimensional superfluid, which represents the onset of rotational superfluidity in small helium droplets.



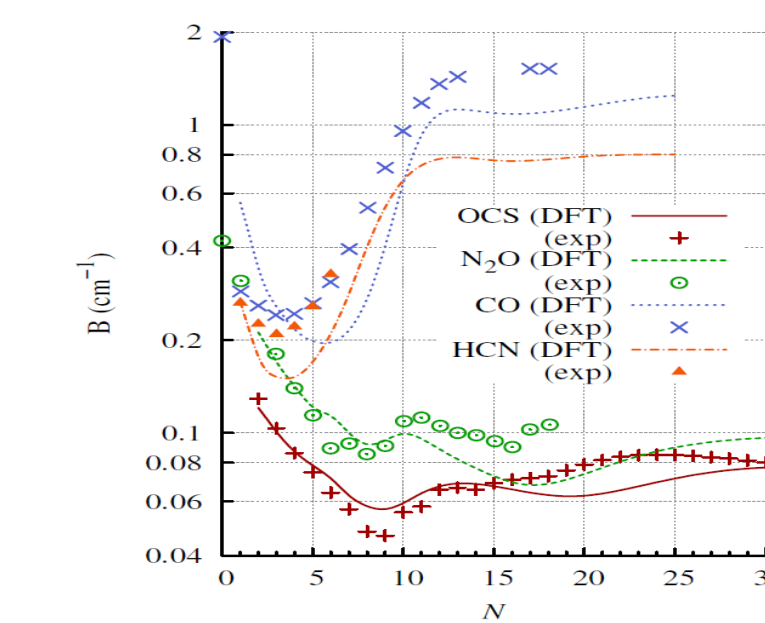
**Figure 4:** Figure caption

## Empirical Methods

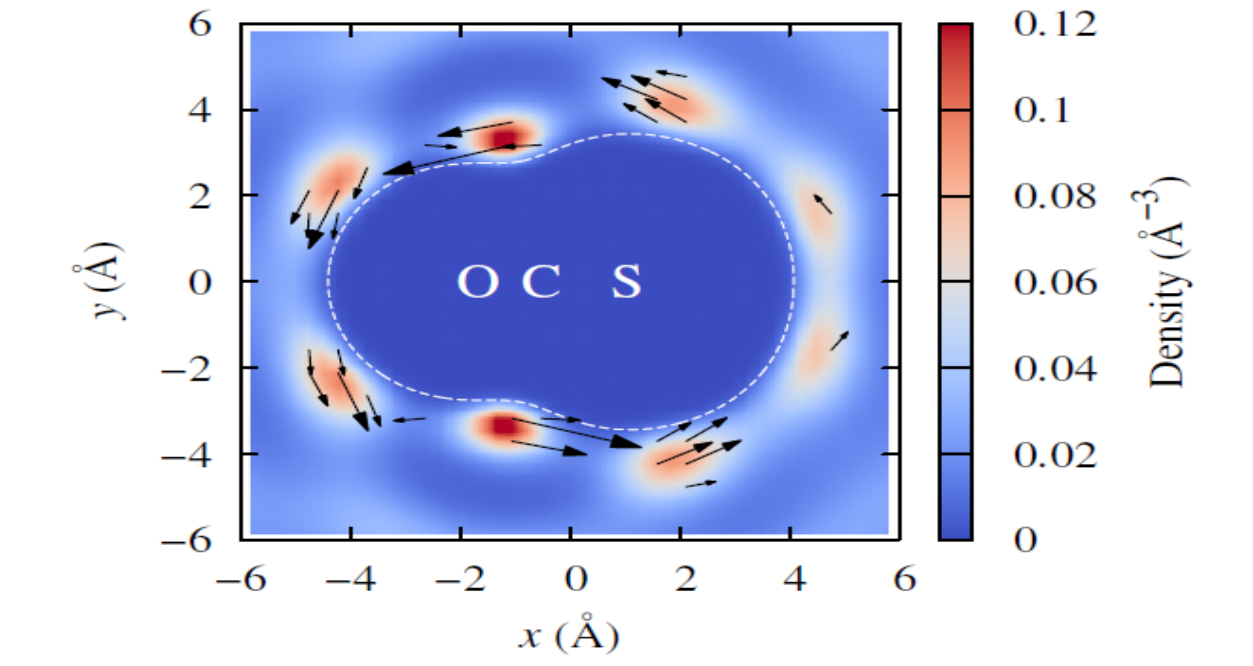
Helium is an interesting element with physical properties that are crucial for understanding its behavior when it takes part in chemical reactions. This element has been known to exist as a gas, liquid and even a solid. In this experiment, the behavior of linear molecules such as OCS (carbonyl sulfide), N<sub>2</sub>O, CO and HCN is observed by using a plot of rotational constant ( $B$ ) vs. number of helium atom ( $N$ ). In this case, small droplets of helium are used as the solvent. Analyzing the effect of helium on these probe molecules is what helps understand the superfluid behavior of helium. The temperature at which <sup>4</sup>He acts as a superfluid is 0.38K. When helium atoms are added to one of these molecules, its rotation gets lowered as it starts getting heavier which is expected (see Fig.1). The strange increase of the rotational constant at  $N=9$  and decrease of moment of inertia becomes evident. This is considered to be the quantum transition of the reaction in which rotational superfluidity is observed.

## Results

In summary, the turnover point in the rotational constants indicate onset of rotational superfluidity. Rotational superfluidity starts when phase coherence occurs meaning that the molecule becomes completely coated with helium atoms. This cause for this quantum effect has more to do with the geometry of the molecule rather than the intrinsic properties of helium. It is important to mention that superfluidity can be described as both rotational and translational superfluidity. The difference between rotation and translation has to do with the change of location for the molecule even though both refer to motion. In addition, the molecule moves at a constant velocity and no vortex is formed in translation superfluidity. Superfluidity for translation occurs at a much higher value of  $N$  than for rotation (see Fig. 3). The alignment of molecules with respect to helium atoms produces rotational wave packets which resemble the behavior of classical rotors. The rotations observed in this analysis can provide relevant information that can help differentiate quantum rotors from classical ones.



**Figure 5:** Plot of rotational constant ( $B$ ) vs number of helium atoms ( $N$ ) for OCS, N<sub>2</sub>O and HCN molecules.



**Figure 6:** Large droplets of helium around OCS which shows a counter-clockwise rotation in 2 dimensions.

## Conclusions

In diam mauris, sagittis ornare est sed, convallis scelerisque eros. Curabitur vel ligula In summary, the turnover point in the rotational constants indicate onset of rotational superfluidity. Rotational superfluidity starts when phase coherence occurs meaning that the molecule becomes completely coated with helium atoms. This cause for this quantum effect has more to do with the geometry of the molecule rather than the intrinsic properties of helium. It is important to mention that superfluidity can be described as both rotational and translational superfluidity. The difference between rotation and translation has to do with the change of location for the molecule even though both refer to motion. In addition, the molecule moves at a constant velocity and no vortex is formed in translation superfluidity. Superfluidity for translation occurs at a much higher value of  $N$  than for rotation (see Fig. 3). The alignment of molecules with respect to helium atoms produces rotational wave packets which resemble the behavior of classical rotors. The rotations observed in this analysis can provide relevant information that can help differentiate quantum rotors from classical ones.

## References

## Forthcoming