Far-from-equilibrium dynamics of molecules in ^{4}He nanodroplets: a quasiparticle perspective

Giacomo Bighin

Institute of Science and Technology Austria

1st Workshop on Molecular Quantum Technology – Puerto Natales, December 19th, 2019

Quantum impurities

One particle (or a few particles) interacting with a many-body environment.

- Condensed matter
- Chemistry
- Ultracold atoms

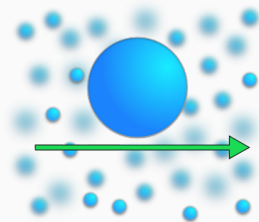How are the properties of the particle modified by the interaction?

$\mathcal{O}(10^{23})$ degrees of freedom.

Quantum impurities

Structureless impurity: translational degrees of freedom/linear momentum exchange with the bath.

Most common cases: electron in a solid, atomic impurities in a BEC.

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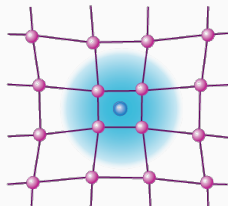

Image from: F. Chevy, Physics **9**, 86.

Quantum impurities

Structureless impurity: translational degrees of freedom/linear momentum exchange with the bath.

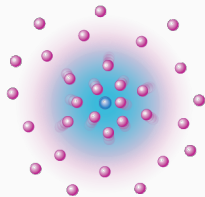Most common cases: electron in a solid, atomic impurities in a BEC.

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Quantum impurities

Structureless impurity: translational degrees of freedom/linear momentum exchange with the bath.

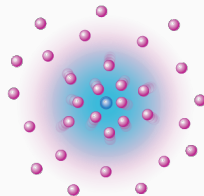Most common cases: electron in a solid, atomic impurities in a BEC.

Image from: F. Chevy, Physics **9**, 86.

Composite impurity (e.g. a molecule): translational *and rotational* degrees of freedom/linear and angular momentum exchange.

Quantum impurities

Structureless impurity: translational degrees of freedom/linear momentum exchange with the bath.

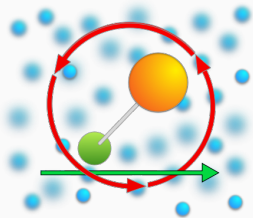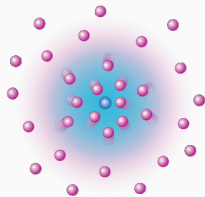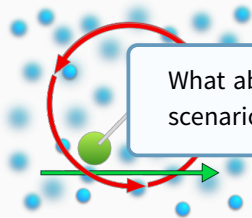Most common cases: electron in a solid, atomic impurities in a BEC.
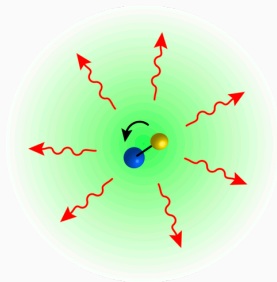

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Composite impurity (e.g. a molecule): of um exchange.

What about a rotating impurity? How can this scenario be realized experimentally?

Strong motivation for the study of composite impurities comes from many different fields. Composite impurities can be realized as:

- Ultracold molecules and ions.

B. Midya, M. Tomza, R. Schmidt, and M. Lemeshko, Phys. Rev. A **94**, 041601(R) (2016).

Strong motivation for the study of composite impurities comes from many different fields. Composite impurities can be realized as:

- Ultracold molecules and ions.

- Rotating molecules inside a 'cage' in perovskites.

T. Chen et al., PNAS **114**, 7519 (2017).
J. Lahnsteiner et al., Phys. Rev. B **94**, 214114 (2016).
Image from: C. Eames et al, Nat. Comm. **6**, 7497 (2015).

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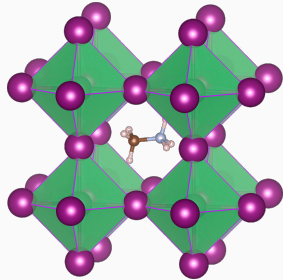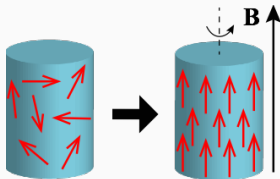
- Ultracold molecules and ions.

- Rotating molecules inside a 'cage' in perovskites.

- Angular momentum transfer from the electrons to a crystal lattice.

J.H. Mentink, M.I. Katsnelson, M. Lemeshko, *"Quantum many-body dynamics of the Einstein-de Haas effect"*, Phys. Rev. B **99**, 064428 (2019).

Composite impurities: where to find them

Strong motivation for the study of composite impurities comes from many different fields. Composite impurities can be realized as:

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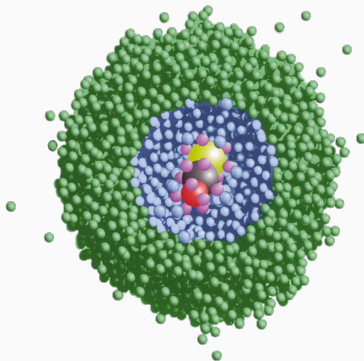- Molecules embedded into helium nanodroplets.

Image from: J. P. Toennies and A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004).

Molecules in helium nanodroplets

A molecular impurity embedded into a helium nanodroplet: a controllable system to explore angular momentum redistribution in a many-body environment.

Temperature ~ 0.4K

Droplets are superfluid

Easy to produce

Free of perturbations

Only rotational degrees of freedom

Easy to manipulate by a laser

Image from: S. Grebenev *et al.*, Science **279**, 2083 (1998).
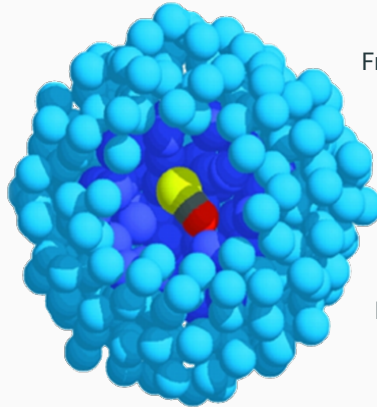
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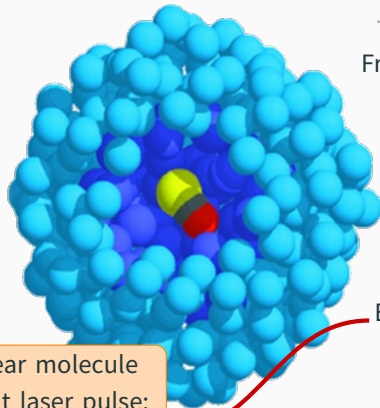

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Interaction of a linear molecule with an off-resonant laser pulse:

$$\hat{H}_{\text{laser}} = -\frac{1}{4}\Delta\alpha E^2(t)\cos^2\hat{\theta}$$

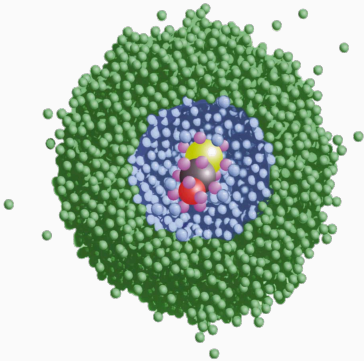Image from: S. Grebenev *et al.*, Science **279**, 2083 (1998).

Molecules embedded into helium nanodroplets: rotational spectrum

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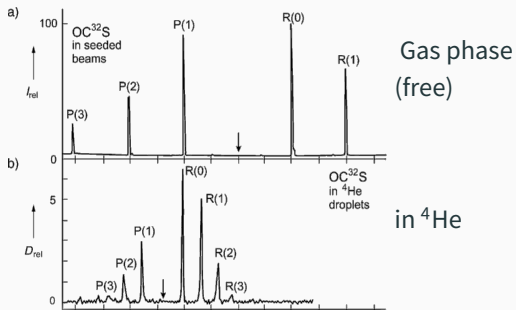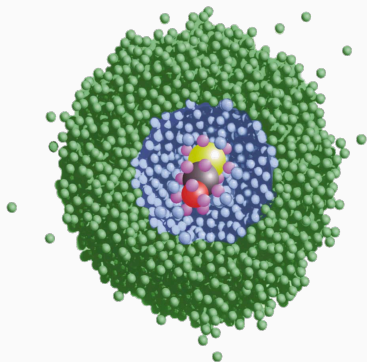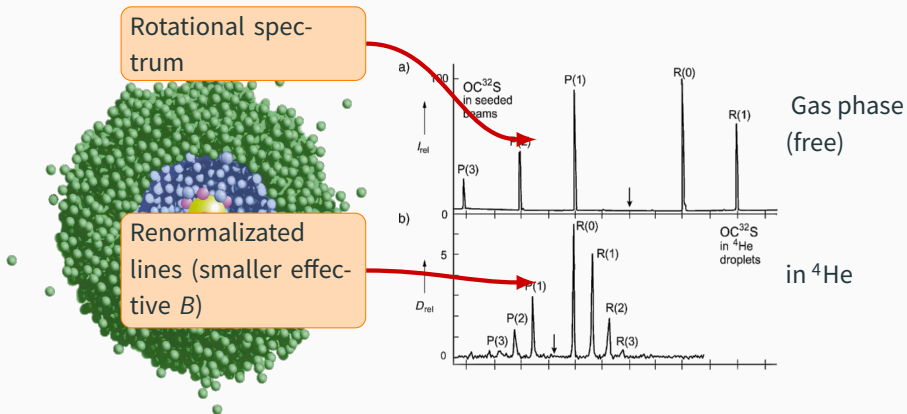Molecules embedded into helium nanodroplets: rotational spectrum

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Molecules embedded into helium nanodroplets: rotational spectrum

Rotational spectrum

Renormalized lines (smaller effective B)

Gas phase (free)

in ^{4}He

Images from: J. P. Toennies and A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004).

Dynamical alignment experiments
(Stapelfeldt group, Aarhus University):

- Kick pulse, aligning the molecule.
- Probe pulse, destroying the molecule.
- Fragments are imaged, reconstructing alignment as a function of time.
- Averaging over multiple realizations, and varying the time between the two pulses, one gets

$$\left\langle \cos^2 \hat{\theta}_{2D} \right\rangle (t)$$

with:

$$\cos^2 \hat{\theta}_{2D} \equiv \frac{\cos^2 \hat{\theta}}{\cos^2 \hat{\theta} + \sin^2 \hat{\theta} \sin^2 \hat{\phi}}$$
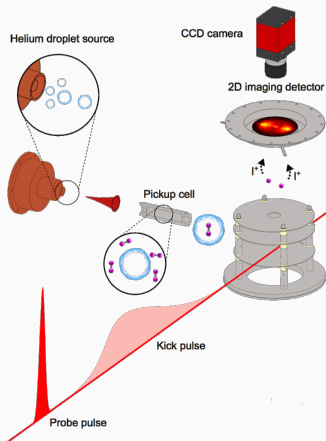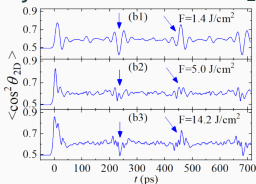

Image from: B. Shepperson *et al.*, Phys. Rev. Lett. **118**, 203203 (2017).
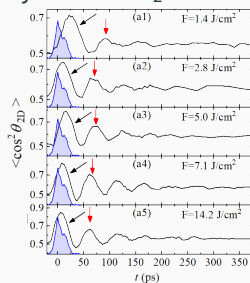
Dynamical alignment of molecules in He nanodroplets

Dynamics of isolated I_2 molecules

Experiment: Henrik Stapelfeldt, Lars Christiansen,
Anders Vestergaard Jørgensen (Aarhus University)

Dynamics of I_2 molecules in helium

Effect of the environment is substantial:

- The peak of prompt alignment doesn't change its shape as the fluence $F = \int dt\, I(t)$ is changed.
- The revival structure differs from the gas-phase: revivals with a 50ps period of unknown origin.
- The oscillations appear weaker at higher fluences.
- An intriguing puzzle: not even a qualitative understanding. Monte Carlo? He-DFT?

Quasiparticle approach

The quantum mechanical treatment of many-body systems is always challenging. How can one simplify the quantum impurity problem?
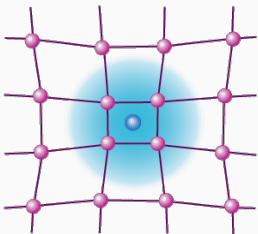
The quantum mechanical treatment of many-body systems is always challenging. How can one simplify the quantum impurity problem?

Polaron: an electron dressed by a field of many-body excitations.

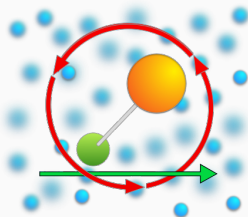**Angulon**: a quantum rotor dressed by a field of many-body excitations.

Image from: F. Chevy, Physics **9**, 86.

The Hamiltonian

A rotating linear molecule interacting with a bosonic bath can be described in the frame co-rotating with the molecule by the following Hamiltonian:

$$\hat{\mathcal{H}} = B(\widehat{\mathbf{L}} - \widehat{\mathbf{\Lambda}})^2 + \sum_{k\lambda\mu} \omega_k \hat{b}^\dagger_{k\lambda\mu} \hat{b}_{k\lambda\mu} + \sum_{k\lambda} V_{k\lambda}(\hat{b}^\dagger_{k\lambda 0} + \hat{b}_{k\lambda 0}),$$

Notation:

- $\widehat{\mathbf{L}}$ the total angular-momentum operator of the combined system, consisting of a molecule and helium excitations.
- $\widehat{\mathbf{\Lambda}}$ is the angular-momentum operator for the bosonic helium bath, whose excitations are described by $\hat{b}_{k\lambda\mu}/\hat{b}^\dagger_{k\lambda\mu}$ operators.
- $k\lambda\mu$: angular momentum basis. k the magnitude of linear momentum of the boson, λ its angular momentum, and μ the z-axis angular momentum projection.
- ω_k gives the dispersion relation of superfluid helium.
- $V_{k\lambda}$ encodes the details of the molecule-helium interactions.

The Hamiltonian

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Compare with the Lee-Low-Pines Hamiltonian

$$\hat{H}_{\mathrm{LLP}} = \frac{\left(\mathbf{P} - \sum_{\mathbf{k}} \mathbf{k} \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \right)^2}{2m_I} + \sum_{\mathbf{k}} \omega_k \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} + \frac{g}{\mathcal{V}} \sum_{\mathbf{k}, \mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'}$$
tions.

Dynamics: time-dependent variational Ansatz

We describe dynamics using a time-dependent variational Ansatz, including excitations up to one phonon:

$$|\psi_{LM}(t)\rangle = \hat{U}(g_{LM}(t)\,|0\rangle_{\text{bos}}\,|LM0\rangle + \sum_{k\lambda n}\alpha_{k\lambda n}^{LM}(t)b_{k\lambda n}^{\dagger}\,|0\rangle_{\text{bos}}\,|LMn\rangle)$$

Lagrangian on the variational manifold defined by $|\psi_{LM}\rangle$:

$$\mathcal{L} = \langle\psi_{LM}|\mathrm{i}\partial_t - \hat{\mathcal{H}}|\psi_{LM}\rangle$$
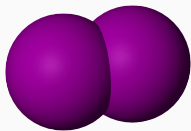
Euler-Lagrange equations of motion:

$$\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{x}_i} - \frac{\partial\mathcal{L}}{\partial x_i} = 0$$

where $x_i = \{g_{LM}, \alpha_{k\lambda n}^{LM}\}$. We obtain a differential system
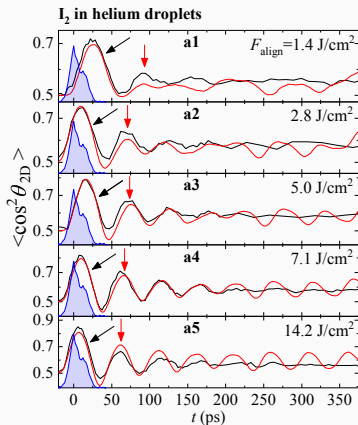
$$\begin{cases} \dot{g}_{LM}(t) = \dots \\ \dot{\alpha}_{k\lambda n}^{LM}(t) = \dots \end{cases}$$

to be solved numerically; in $\alpha_{k\lambda\mu}$ the momentum k needs to be discretized.

Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: I_2.
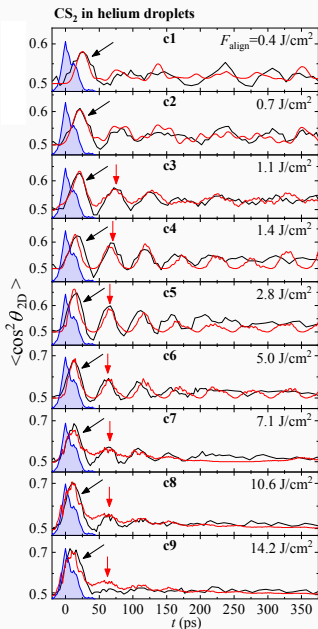

I_2 in helium droplets

Generally good agreement for the main features in experimental data:

- Oscillations with a period of 50ps, growing in amplitude as the laser fluence is increased.

- Oscillations decay: at most 4 periods are visible.

- The width of the first peak does not change much with fluence.

—— Experiment   Laser pulse
—— Angulon theory

CS$_2$ in helium droplets

Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: CS_2.
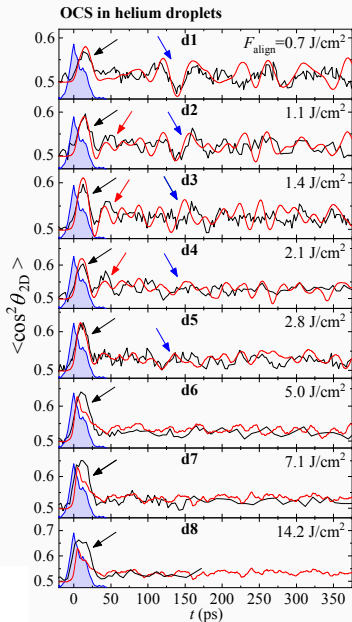

- Again, a persistent oscillatory pattern.
- For higher values of the fluence the oscillatory pattern disappears.

— Experiment   ▨ Laser pulse
— Angulon theory

OCS in helium droplets

Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: OCS.
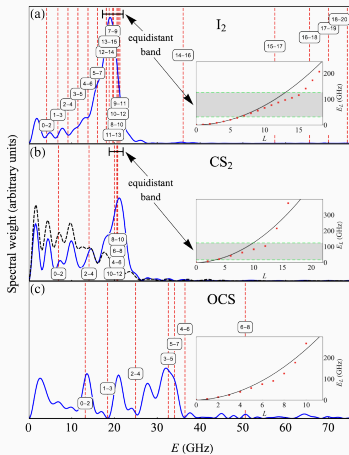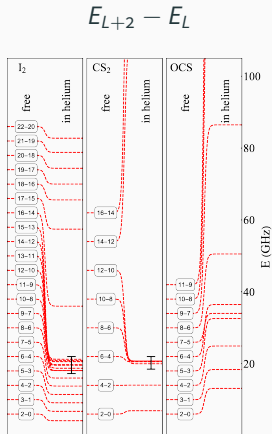
- Unfortunately the data is noisier.
- Oscillatory pattern not present, except in a couple of cases where one weak oscillation might be identified.
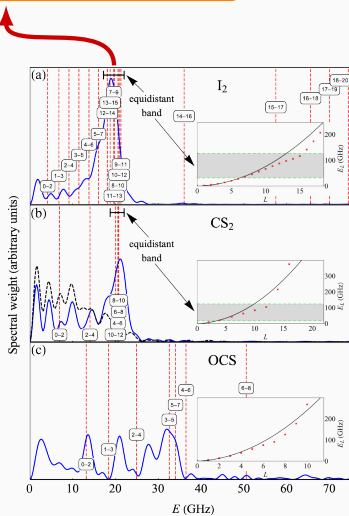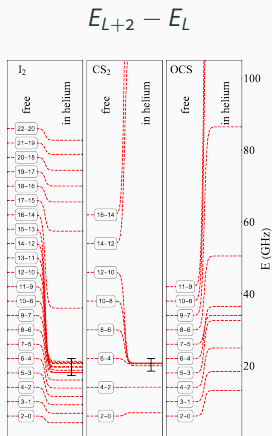
—— Experiment
—— Angulon theory

Laser pulse

The Fourier transform of the measured alignment cosine $\langle \cos^2 \hat{\theta}_{2D} \rangle(t)$ is dominated by $(L) \leftrightarrow (L+2)$ interferences. How is it affected when the level structure changes?
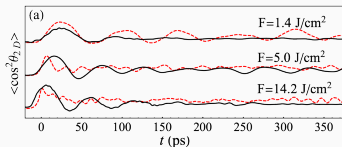

$E_{L+2} - E_L$

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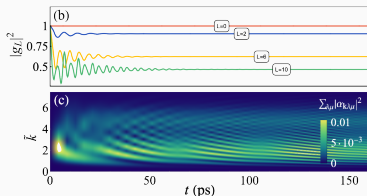
20Ghz corresponds to 50ps

$$E_{L+2} - E_L$$

i) Is this the full story? Can the observed dynamics be explained only by means of renormalised rotational levels?

Red dashed lines (only renormalised levels) vs. solid black line (full many-body treatment).

ii) How long does it take for a molecule to equilibrate with the helium environment and form an angulon quasiparticle? This requires tens of ps; which is also the timescale of the laser!

Approach to equilibrium of the quasiparticle weight $|g_{LM}|^2$ and of the phonon populations $\sum_k |\alpha_{k\lambda\mu}|^2$.

i) Is this the fu
dynamics be
renormalised

ii) How long d
equilibrate w
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timescale of t

With a shorter 450 fs pulse, same molecule (I_2), the strong oscillatory pattern is absent:
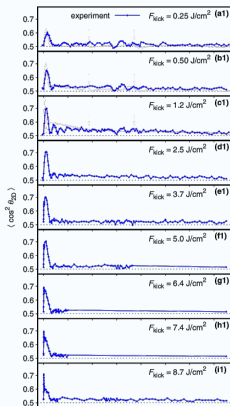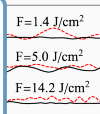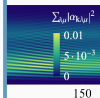

F=1.4 J/cm²
F=5.0 J/cm²
F=14.2 J/cm²
300   350

d levels) vs.
atment).

L=10

$\sum_{k,u} |\alpha_{k,u}|^2$
0.01
$5 \cdot 10^{-3}$
0
150

siparticle
opulations

Image from: B. Shepperson *et al.*, Phys. Rev. Lett. **118**, 203203 (2017).

Conclusions

- A novel kind of pump-probe spectroscopy, based on impulsive molecular alignment in the laboratory frame, providing access to the structure of highly excited rotational states.

- Superfluid bath leads to formation of robust long-wavelength oscillations in the molecular alignment; an explanation requires a many-body theory of angular momentum redistribution.

- Our theoretical model allows us to interpret this behavior in terms of the dynamics of angulon quasiparticles, shedding light onto many-particle dynamics of angular momentum at femtosecond timescales.

- Future perspectives:
  - All molecular geometries (spherical tops, asymmetric tops).
  - Optical centrifuges and superrotors.
  - Can a rotating molecule create a vortex?

- For more details: arXiv:1906.12238

Lemeshko group @ IST Austria:

Misha Lemeshko

Dynamics in He

Enderalp Yakaboylu

Xiang Li

Igor Cherepanov

Wojciech Rządkowski

Collaborators:

Henrik Stapelfeldt (Aarhus)

Richard Schmidt (MPI Garching)

Dynamical alignment experiments

Thank you for your attention.

These slides at http://bigh.in