

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

Giacomo Bighin

Institute of Science and Technology Austria

Universidade Federal do Rio Grande do Norte — Natal, April 16th, 2020

Quantum impurities

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

- Condensed matter
- Chemistry
- Ultracold atoms: tunable interaction with either bosons or fermions.

A prototype of a many-body system.

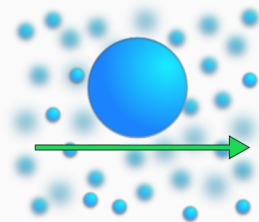
How are the properties of the particle modified by the interaction?



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.



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.

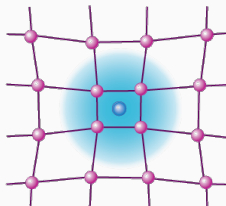


Image from: F. Chevy, Physics 9, 86.

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.

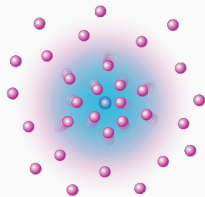


Image from: F. Chevy, Physics 9, 86.

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.**

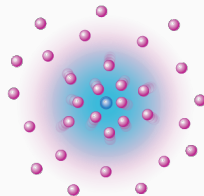
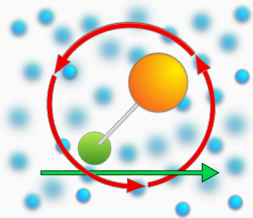


Image from: F. Chevy, Physics 9, 86.



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.**

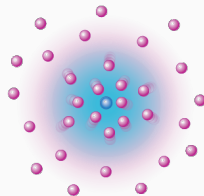
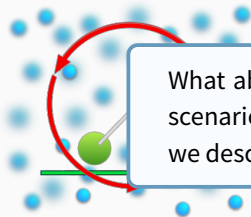


Image from: F. Chevy, Physics 9, 86.

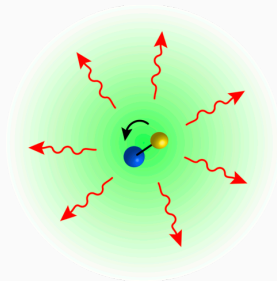


What about a **rotating impurity**? How can this scenario be realized experimentally? How can we describe it?

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:

- **Ultracold molecules** and ions.

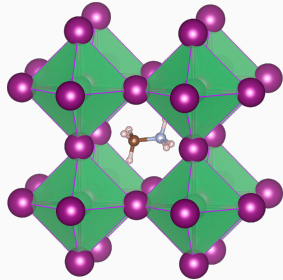


B. Midya, M. Tomza, R. Schmidt, and M. Lemeshko, Phys. Rev. A **94**, 041601(R) (2016).

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:

- **Ultracold molecules** and ions.
- Rotating molecules inside a 'cage' in **perovskites**.



T. Chen et al., PNAS **114**, 7519 (2017).

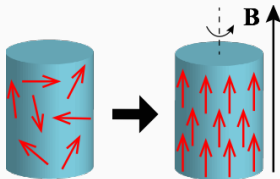
J. Lahnsteiner et al., Phys. Rev. B **94**, 214114 (2016).

Image from: C. Eames et al, Nat. Comm. **6**, 7497 (2015).

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:

- 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:

- **Ultracold molecules** and ions.
- Rotating molecules inside a 'cage' in **perovskites**.
- Angular momentum transfer from the **electrons** to a **crystal lattice**.
- **Molecules** embedded into **helium nanodroplets**.

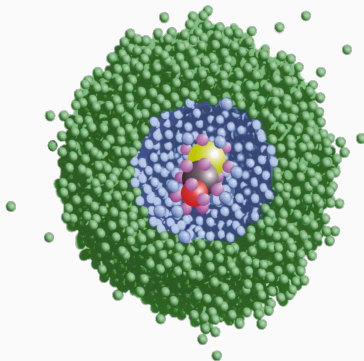


Image from: J. P. Toennies and A. F. Vilesov, *Angew. Chem. Int. Ed.* **43**, 2622 (2004).

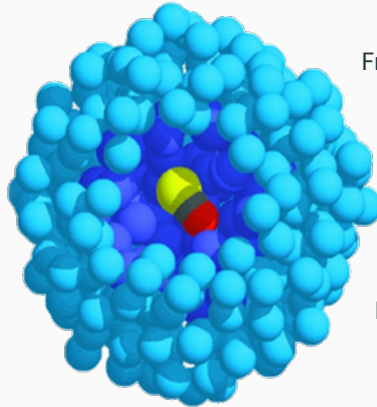
Molecules in helium nanodroplets

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

Temperature $\sim 0.4\text{K}$

Droplets are
superfluid

Easy to produce



Free of perturbations

Only rotational
degrees of freedom

Easy to manipulate
by a laser

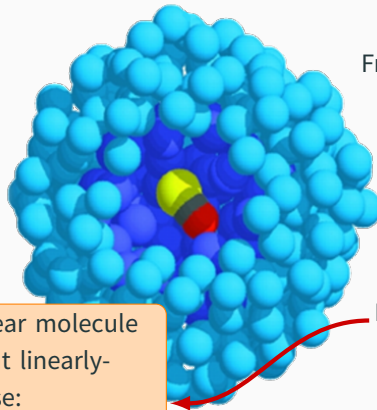
Image from: S. Grebenev *et al.*,
Science **279**, 2083 (1998).

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 $\sim 0.4\text{K}$

Droplets are superfluid



Free of perturbations

Only rotational degrees of freedom

Easy to manipulate by a laser

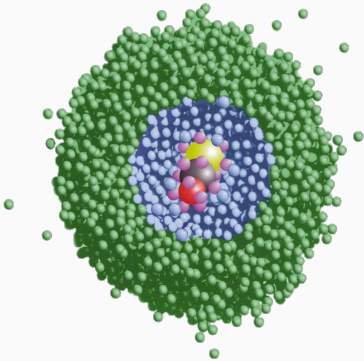
Interaction of a linear molecule with an off-resonant linearly-polarized laser pulse:

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

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

Rotational spectrum of molecules in He nanodroplets

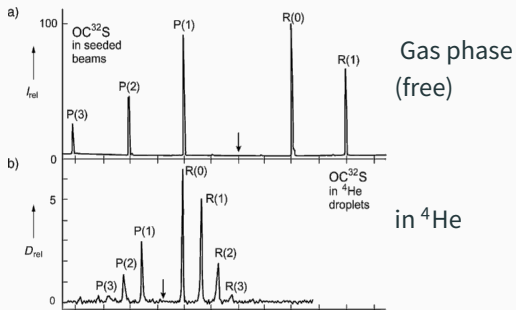
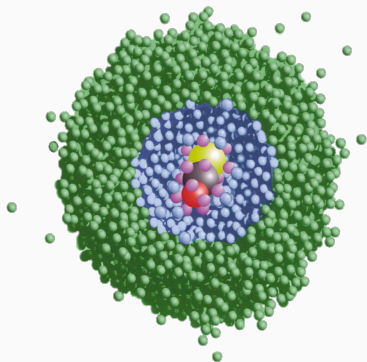
Molecules embedded into helium nanodroplets: rotational spectrum



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

Rotational spectrum of molecules in He nanodroplets

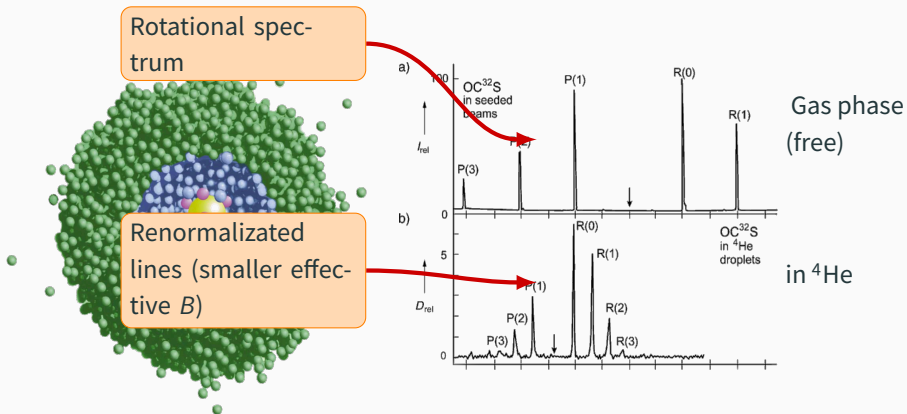
Molecules embedded into helium nanodroplets: rotational spectrum



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

Rotational spectrum of molecules in He nanodroplets

Molecules embedded into helium nanodroplets: rotational spectrum



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

Dynamical alignment of molecules in He nanodroplets

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

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

with:

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

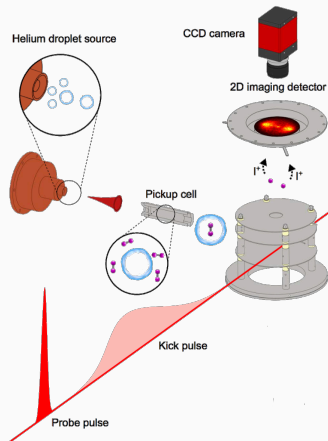


Image from: B. Shepperson *et al.*, Phys. Rev. Lett. **118**, 203203 (2017).

Dynamical alignment of molecules in He nanodroplets

A simpler example: a **free** molecule interacting with an off-resonant laser pulse

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

When acting on a **free molecule**, the laser excites in a short time many rotational states ($L \leftrightarrow L + 2$), creating a **rotational wave packet**:

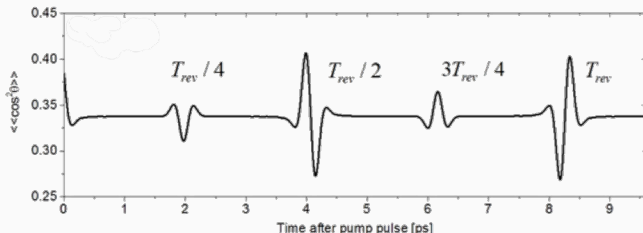
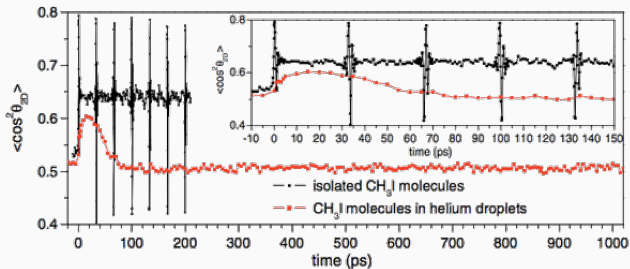


Image from: G. Kaya *et al.*, Appl. Phys. B 6, 122 (2016).

Movie

Dynamical alignment of molecules in He nanodroplets

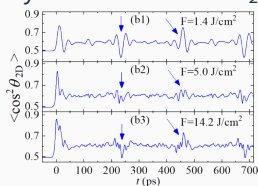
Effect of the environment is substantial: **free molecule** vs. **same molecule in He**.



Stapelfeldt group, Phys. Rev. Lett. **110**, 093002 (2013).

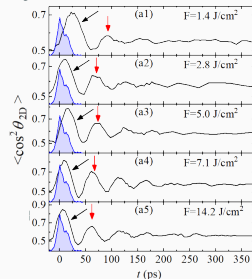
Dynamical alignment of molecules in He nanodroplets

Dynamics of isolated I_2 molecules



Experiment: Stapelfeldt group (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?

Quasiparticle approach

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.

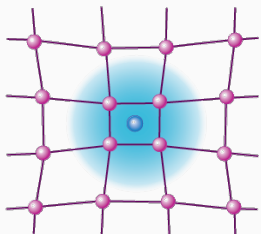
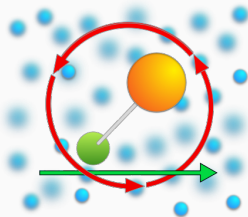


Image from: F. Chevy, *Physics* **9**, 86.

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



R. Schmidt and M. Lemeshko, *Phys. Rev. Lett.* **114**, 203001 (2015).

R. Schmidt and M. Lemeshko, *Phys. Rev. X* **6**, 011012 (2016).

Yu. Shchadilova, "Viewpoint: A New Angle on Quantum Impurities", *Physics* **10**, 20 (2017).

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:

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

Notation:

- $\hat{\mathbf{L}}$ the total angular-momentum operator of the combined system, consisting of a molecule and helium excitations.
- $\hat{\mathbf{A}}$ is the angular-momentum operator for the bosonic helium bath, whose excitations are described by $\hat{b}_{k\lambda\mu}/\hat{b}_{k\lambda\mu}^\dagger$ 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

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

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

Notation:

- $\hat{\mathbf{L}}$ the total angular-momentum operator of the combined system, consisting of a molecule and helium excitations.
- $\hat{\mathbf{\Lambda}}$ is the angular-momentum operator for the bosonic helium bath, whose excitations are described by $\hat{b}_{k\lambda\mu}/\hat{b}_{k\lambda\mu}^\dagger$ operators.
- $k\lambda\mu$: angular momentum basis. k the magnitude of linear momentum of

Compare with the Lee-Low-Pines Hamiltonian

$$\hat{H}_{\text{LLP}} = \frac{\left(\mathbf{P} - \sum_{\mathbf{k}} \mathbf{k} \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}}\right)^2}{2m_I} + \sum_{\mathbf{k}} \omega_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + \frac{g}{\mathcal{V}} \sum_{\mathbf{k}, \mathbf{k}'} \hat{b}_{\mathbf{k}'}^\dagger \hat{b}_{\mathbf{k}}$$

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 $|\psi_{LM}\rangle$:

$$\mathcal{L} = \langle \psi_{LM} | i\partial_t - \hat{\mathcal{H}} | \psi_{LM} \rangle$$

Euler-Lagrange **equations of motion**:

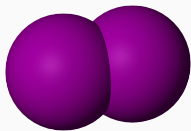
$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = 0$$

where $x_i = \{g_{LM}, \alpha_{k\lambda n}^{LM}\}$. We obtain a **differential system**

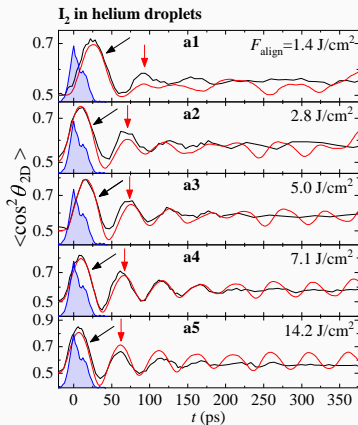
$$\begin{cases} \dot{g}_{LM}(t) = \dots \\ \dot{\alpha}_{k\lambda n}^{LM}(t) = \dots \end{cases}$$

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

Theory vs. experiments: I_2



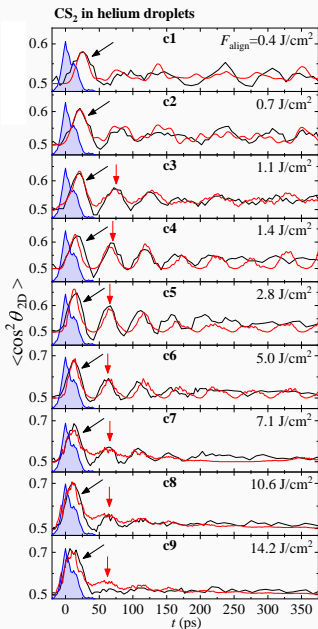
Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: I_2 .



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.

Theory vs. experiments: CS₂



Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: CS₂.

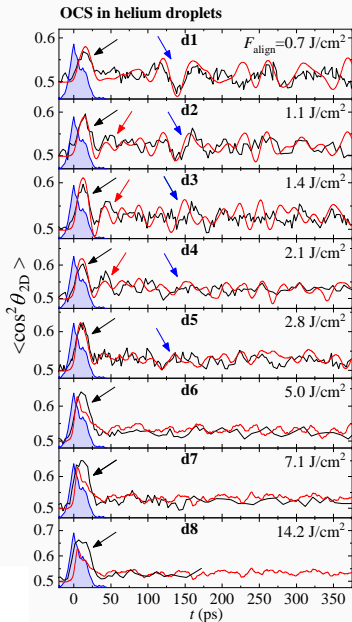


- Again, a persistent oscillatory pattern.
- For higher values of the fluence the oscillatory pattern disappears.

— Experiment Laser pulse

— Angulon theory

Theory vs. experiments: OCS



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 Laser pulse
— Angulon theory

- Can we shed light on the origin of oscillations? Why the 50ps period? Why do they sometimes disappear? What about the decay?



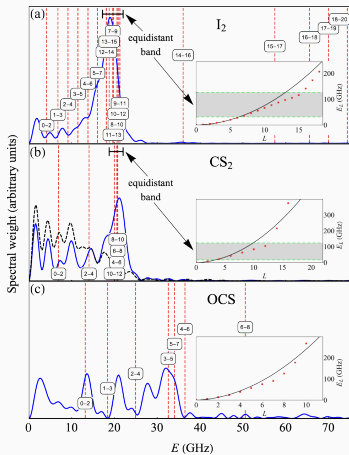
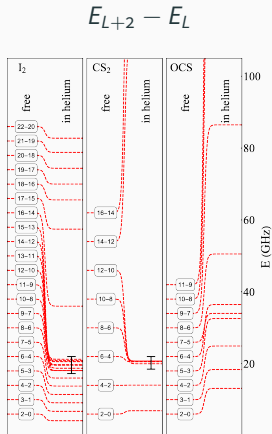
- Can we shed light on the origin of oscillations? Why the 50ps period? Why do they sometimes disappear? What about the decay?



- A microscopical theory allows us to reconstruct the pathways of angular momentum redistribution: **microscopical insight** on the problem!
 - We can fully characterize the helium excitations dressing by the molecule.
 - At the same we can also analyze how molecular properties (populations, energy levels) are affected by the many-body environment.

Experiments vs. theory: spectrum

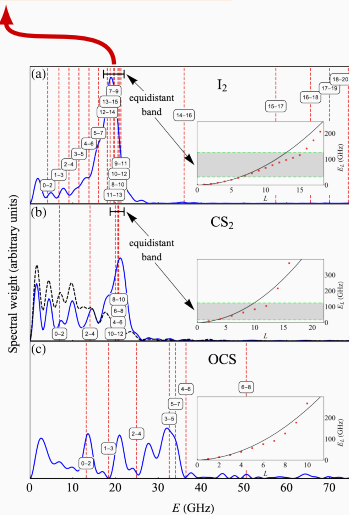
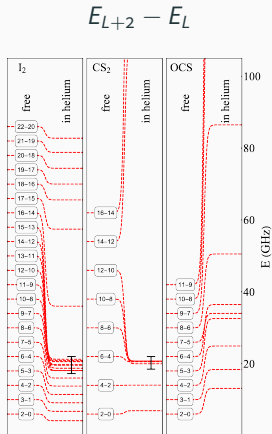
The Fourier transform of the measured alignment cosine $\langle \cos^2 \hat{\theta}_{2D} \rangle(t)$ is dominated by $(L) \leftrightarrow (L + 2)$ interferences. How is it affected when the level structure changes?



Experiments vs. theory: spectrum

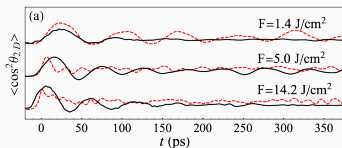
The Fourier transform of the measured alignment cosine $\langle \cos^2 \hat{\theta}_{2D} \rangle(t)$ is dominated by $(L) \leftrightarrow (L + 2)$ interferences. How is it affected when the level structure changes?

20GHz corresponds to 50ps



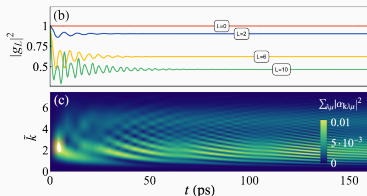
Many-body dynamics of angular momentum

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 $\sum_k |\alpha_{k\lambda\mu}|^2$.

Many-body dynamics of angular momentum

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

i) Is this the full
dynamics be
renormalised

ii) How long do
equilibrate with
and form an a
requires tens
timescale of t

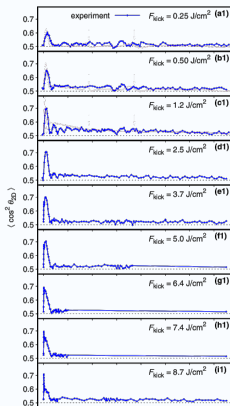
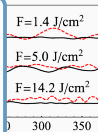


Image from: B. Shepperson *et al.*, Phys. Rev. Lett. **118**, 203203 (2017).



d levels) vs.
treatment).



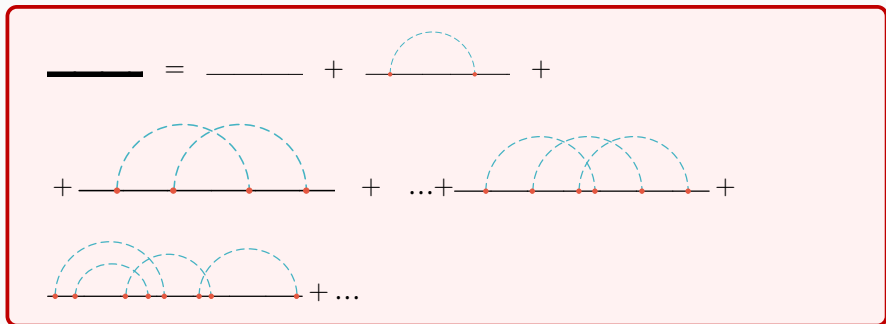
disparticle
populations

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](https://arxiv.org/abs/1906.12238)

Diagrammatic Monte Carlo

More numerical approach: **DiagMC**, sampling all diagrams in a stochastic way.



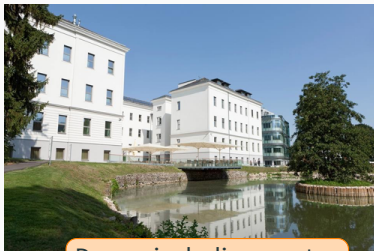
How do we describe angular momentum redistribution in terms of diagrams?
How does the configuration space look like?

Can we use DiagMC to describe a molecule?

Lemeshko group @ IST Austria:



Institute of Science and Technology



Dynamical alignment experiments



Misha
Lemeshko

Dynamics in He



Enderalp
Yakaboylu



Xiang Li



Igor
Cherepanov



Wojciech
Rządowski

Collaborators:



Henrik
Stapelfeldt
(Aarhus)



Richard
Schmidt
(MPQ)



Timur
Tscherbul 22/23
(Reno)

DiagMC

Thank you for your attention.



Der Wissenschaftsfonds.

This work was supported by a Lise Meitner Fellowship of the Austrian Science Fund (FWF), project Nr. M2461-N27.

These slides at <http://bigh.in>

Backup slide # 1: finite-temperature dynamics

For the **impurity**: average over a statistical ensemble, weights $\propto \exp(-\beta E_L)$.

For the **bath**: the zero-temperature bosonic expectation values in \mathcal{L} are converted to finite temperature ones^{1,2}.

$$\mathcal{L}_{T=0} = \langle 0 | \hat{O}^\dagger (i\partial_t - \hat{\mathcal{H}}) \hat{O} | 0 \rangle_{\text{bos}} \longrightarrow \mathcal{L}_T = \text{Tr} \left[\rho_0 \hat{O}^\dagger (i\partial_t - \hat{\mathcal{H}}) \hat{O} \right]$$

[1] A. R. DeAngelis and G. Gatoff, Phys. Rev. C **43**, 2747 (1991).

[2] W.E. Liu, J. Levinsen, M. M. Parish, “*Variational approach for impurity dynamics at finite temperature*”, arXiv:1805.10013

Backup slide # 1: finite-temperature dynamics

For the **impurity**: average over a statistical ensemble, weights $\propto \exp(-\beta E_L)$.

For the **bath**: the zero-temperature bosonic expectation values in \mathcal{L} are converted to finite temperature ones^{1,2}.

$$\mathcal{L}_{T=0} = \langle 0 | \hat{O}^\dagger (i\partial_t - \hat{\mathcal{H}}) \hat{O} | 0 \rangle_{\text{bos}} \longrightarrow \mathcal{L}_T = \text{Tr} \left[\rho_0 \hat{O}^\dagger (i\partial_t - \hat{\mathcal{H}}) \hat{O} \right]$$

A couple of additional details:

- The laser changes the total angular momentum of the system. An appropriate **wavefunction** is then $|\Psi\rangle = \sum_{LM} |\psi_{LM}\rangle$
- **Focal averaging**, accounting for the fact that the laser is not always perfectly focused.
- States with odd/even angular momenta may have **different abundances**, due to the nuclear spin.

[1] A. R. DeAngelis and G. Gatoff, Phys. Rev. C **43**, 2747 (1991).

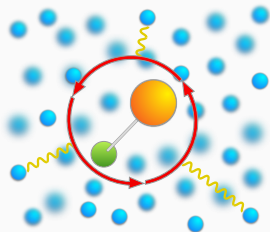
[2] W.E. Liu, J. Levinsen, M. M. Parish, “*Variational approach for impurity dynamics at finite temperature*”, arXiv:1805.10013

Backup slide # 2: the angulon

A composite impurity in a bosonic environment can be described by the angulon Hamiltonian^{1,2,3,4} (angular momentum basis: $\mathbf{k} \rightarrow \{k, \lambda, \mu\}$):

$$\hat{H} = \underbrace{B\hat{J}^2}_{\text{molecule}} + \underbrace{\sum_{k\lambda\mu} \omega_k \hat{b}_{k\lambda\mu}^\dagger \hat{b}_{k\lambda\mu}}_{\text{phonons}} + \underbrace{\sum_{k\lambda\mu} U_\lambda(k) \left[Y_{\lambda\mu}^*(\hat{\theta}, \hat{\phi}) \hat{b}_{k\lambda\mu}^\dagger + Y_{\lambda\mu}(\hat{\theta}, \hat{\phi}) \hat{b}_{k\lambda\mu} \right]}_{\text{molecule-phonon interaction}}$$

- Linear molecule.
- Derived rigorously for a molecule in a weakly-interacting BEC¹.
- Phenomenological model for a molecule in any kind of bosonic bath³.



¹R. Schmidt and M. Lemeshko, Phys. Rev. Lett. **114**, 203001 (2015).

²R. Schmidt and M. Lemeshko, Phys. Rev. X **6**, 011012 (2016).

³M. Lemeshko, Phys. Rev. Lett. **118**, 095301 (2017).

⁴Yu. Shchadilova, "Viewpoint: A New Angle on Quantum Impurities", Physics **10**, 20 (2017).

Backup slide # 2: the angulon

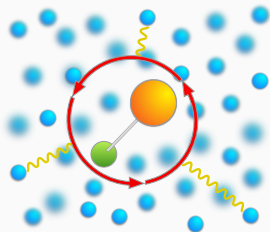
A composite impurity in a bosonic environment can be described by the angulon Hamiltonian^{1,2,3,4} (angular momentum basis: $\mathbf{k} \rightarrow \{k, \lambda, \mu\}$):

$$\hat{H} = \underbrace{B\hat{J}^2}_{\text{molecule}} + \underbrace{\sum_{k\lambda\mu} \omega_k \hat{b}_{k\lambda\mu}^\dagger \hat{b}_{k\lambda\mu}}_{\text{phonons}} + \underbrace{\sum_{k\lambda\mu} U_\lambda(k) \left[Y_{\lambda\mu}^*(\hat{\theta}, \hat{\phi}) \hat{b}_{k\lambda\mu}^\dagger + Y_{\lambda\mu}(\hat{\theta}, \hat{\phi}) \hat{b}_{k\lambda\mu} \right]}_{\text{molecule-phonon interaction}}$$

$\lambda = 0$: spherically symmetric part.

$\lambda \geq 1$ anisotropic part.

- [unclear] a molecule in a weakly-interacting BEC¹.
- Phenomenological model for a molecule in any kind of bosonic bath³.



¹R. Schmidt and M. Lemeshko, Phys. Rev. Lett. **114**, 203001 (2015).

²R. Schmidt and M. Lemeshko, Phys. Rev. X **6**, 011012 (2016).

³M. Lemeshko, Phys. Rev. Lett. **118**, 095301 (2017).

⁴Yu. Shchadilova, "Viewpoint: A New Angle on Quantum Impurities", Physics **10**, 20 (2017).

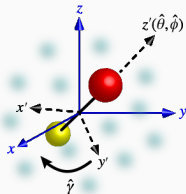
Backup slide # 3: canonical transformation

We apply a canonical transformation

$$\hat{S} = e^{-i\hat{\phi} \otimes \hat{\Lambda}_z} e^{-i\hat{\theta} \otimes \hat{\Lambda}_y} e^{-i\hat{\gamma} \otimes \hat{\Lambda}_x}$$

where $\hat{\Lambda} = \sum_{\mu\nu} b_{k\lambda\mu}^\dagger \vec{\sigma}_{\mu\nu} b_{k\lambda\nu}$ is the angular momentum of the bosons.

Cfr. the Lee-Low-Pines transformation for the polaron.



Bosons: laboratory frame (x, y, z)
Molecule: rotating frame (x', y', z')
defined by the Euler angles $(\hat{\phi}, \hat{\theta}, \hat{\gamma})$.



laboratory frame



rotating frame