Rotational coherence spectroscopy and far-from-equilibrium dynamics of molecules in ^{4}He nanodroplets

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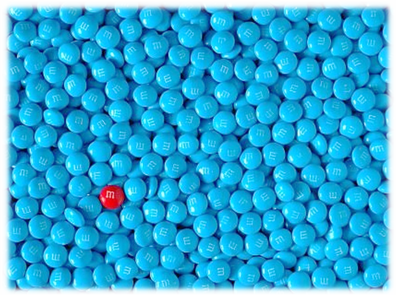
Quantum impurities

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

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



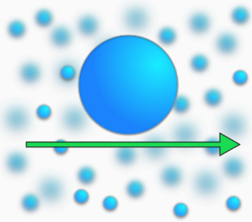
A prototype of a many-body system.

How are the properties of the impurity 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.



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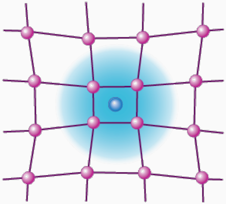

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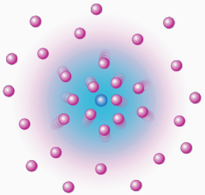

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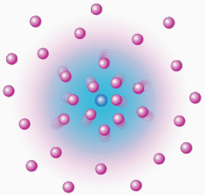

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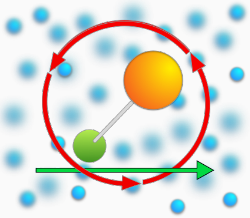

Composite impurity (e.g. a molecule): translational *and rotational* degrees of freedom/linear and angular momentum exchange.

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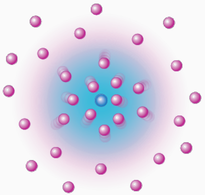

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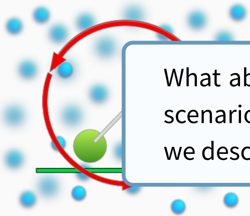


What about a rotating impurity? How can this scenario be realized experimentally? How can we describe it?

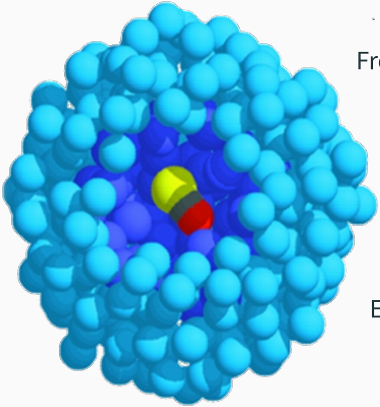
Molecules in helium nanodroplets

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

Temperature $\sim 0.4K$

Droplets are superfluid

Easy to produce



Free of perturbations

Only rotational degrees of freedom

Easy to manipulate by a laser

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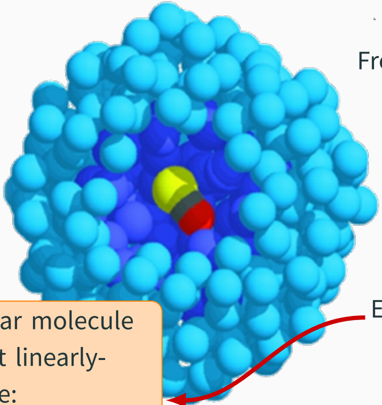

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Easy to manipulate by a laser

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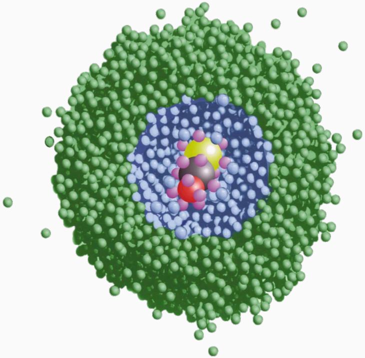
Interaction of a linear molecule with an off-resonant linearly-polarized laser pulse:

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

Rotational spectrum of molecules in He nanodroplets

Molecules embedded into helium nanodroplets: rotational spectrum



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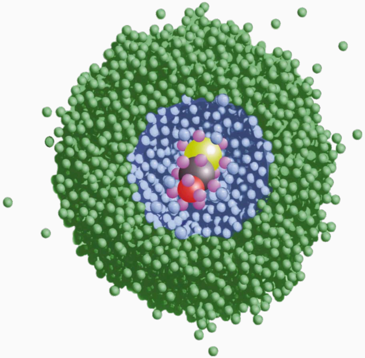

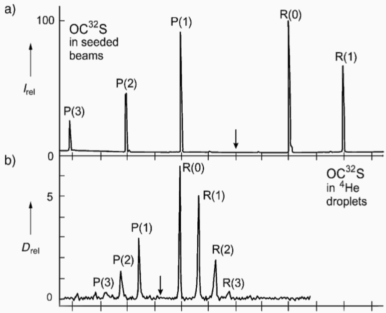

Gas phase (free)

in ^{4}He

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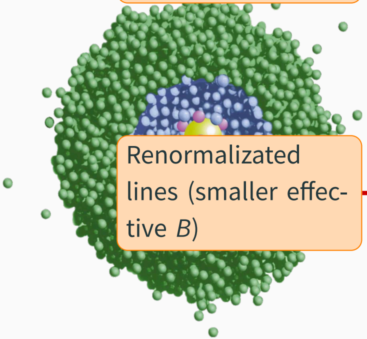
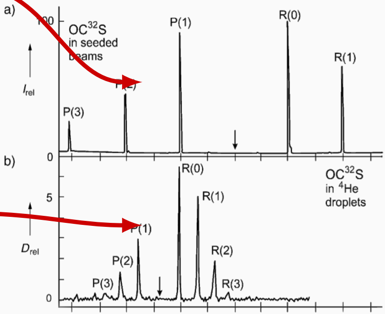
Rotational spectrum



Renormalizated lines (smaller effective B)



Gas phase (free)

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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

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

with:

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

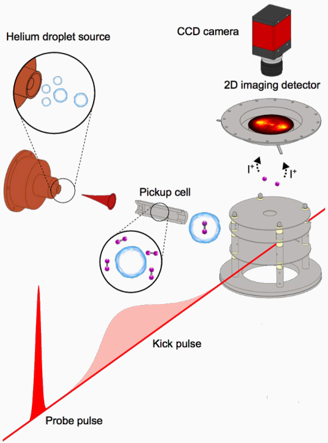
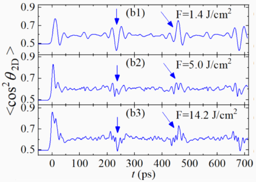


Image from: B. Shepperson *et al.*, Phys. Rev. Lett. **118**, 203203 (2017).

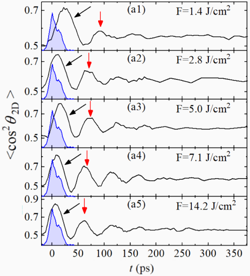
Dynamical alignment of molecules in He nanodroplets

Dynamics of gas phase (free) 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

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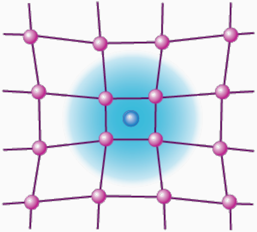
Polaron: an electron dressed by a field of many-body excitations.



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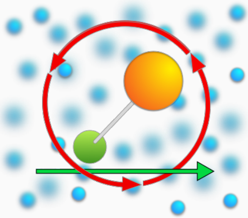
Angulon: a quantum rotor dressed by a field of many-body excitations.



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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:

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

Notation:

- $\widehat{\mathbf{L}}$ the total angular-momentum operator of the combined system, consisting of a molecule and helium excitations.
- $\hat{\Lambda}$ 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.

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Compare with the Lee-Low-Pines Hamiltonian

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

Dynamics: time-dependent variational Ansatz

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

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

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:

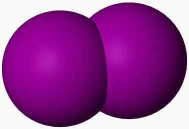
$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = 0$$

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

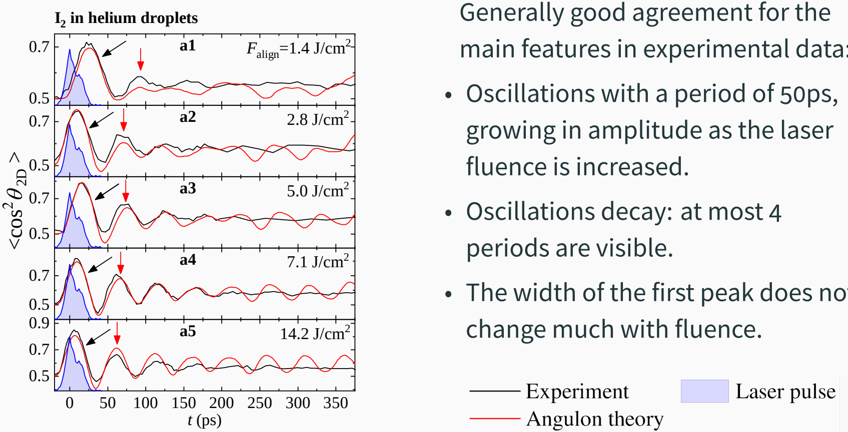
$$\begin{cases} \dot{g}_{LM}(t) = \dots \\ \dot{\alpha}^{LM}_{k\lambda n}(t) = \dots \end{cases}$$

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

Theory vs. experiments: I_2



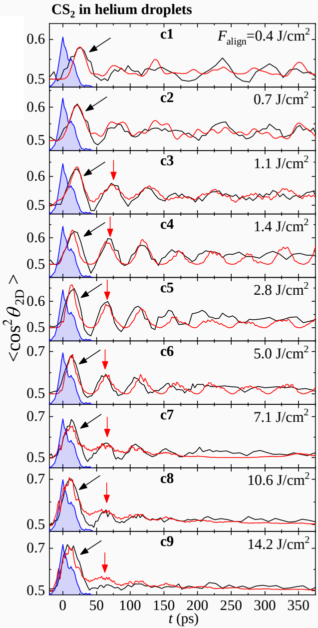
Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: I_2.



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: CS_2



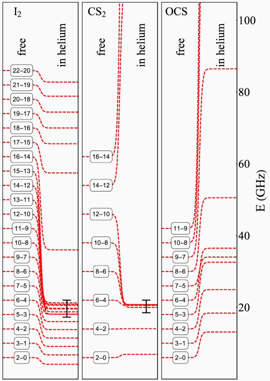
Comparison with experimental data from Stapelfeldt group, Aarhus University, for different molecules: CS_2.

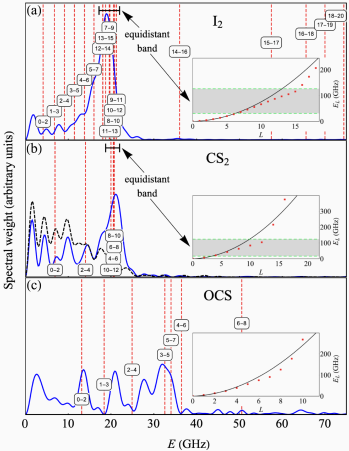
- Again, a persistent oscillatory pattern.
- For higher values of the fluence the oscillatory pattern disappears.

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?

$E_{L+2} - E_L$





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20Ghz corresponds to 50ps

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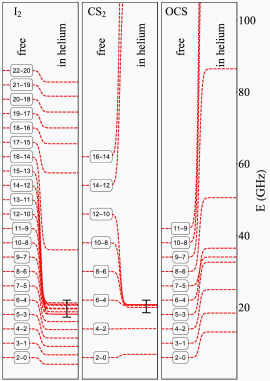
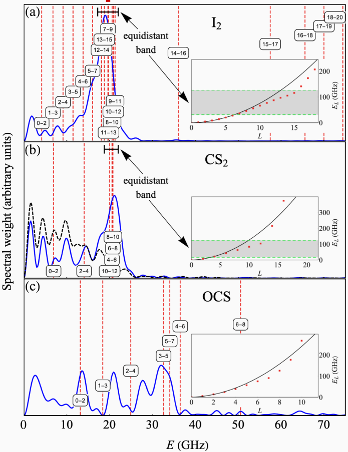
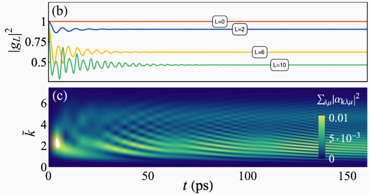




Many-body dynamics of angular momentum

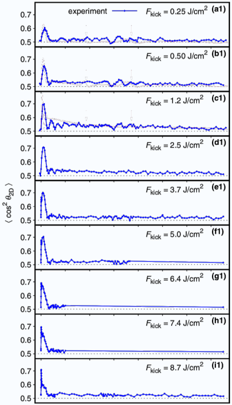
How long does it take for a molecule to equilibrate with the helium environment and form an angulon quasiparticle?
This requires tens of ps; which is also the timescale of the laser!



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:



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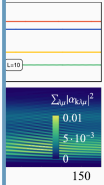

siparticle
opulations

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.
- 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. See also A.S. Chatterley, L. Christiansen, C.A. Schouder, A.V. Jørgensen, B. Shepperson, I.N. Cherepanov, GB, R.E. Zillich, M. Lemeshko, H. Stapelfeldt, *“Rotational coherence spectroscopy of molecules in helium nanodroplets: Reconciling the time and the frequency domains”*, Phys. Rev. Lett., in press.

Lemeshko group @ IST Austria:

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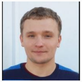
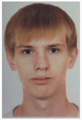


Misha Lemeshko

Dynamics in He

Enderalp Yakaboylu

Xiang Li



Igor Cherepanov

Wojciech Rządkowski

Collaborators:

Dynamical alignment experiments

Henrik Stapelfeldt (Aarhus)

Richard Schmidt (MPQ

Timur Tscherbul (Reno)

Thank you for your attention.

Der Wissenschaftsfonds.

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These slides at http://bigh.in

Backup slide # 1: finite-temperature dynamics

For the impurity: average over a statistical ensamble, 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].

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

[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

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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).
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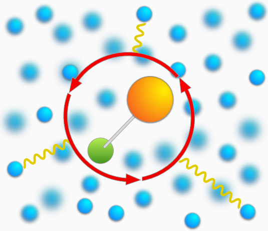
Backup slide # 2: the angulon

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

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

- Linear molecule.
- Derived rigorously for a molecule in a weakly-interacting BEC[1].
- Phenomenological model for a molecule in any kind of bosonic bath[3].



[1] R. Schmidt and M. Lemeshko, Phys. Rev. Lett. **114**, 203001 (2015).
[2] R. Schmidt and M. Lemeshko, Phys. Rev. X **6**, 011012 (2016).
[3] M. Lemeshko, Phys. Rev. Lett. **118**, 095301 (2017).
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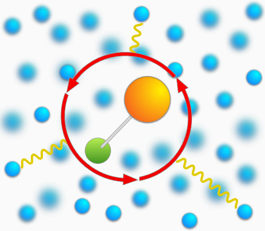
$\lambda = 0$: spherically symmetric part.
$\lambda \geq 1$ anisotropic part.

- L
- D a molecule in a weakly-interacting BEC[1].
- Phenomenological model for a molecule in any kind of bosonic bath[3].



[1] R. Schmidt and M. Lemeshko, Phys. Rev. Lett. **114**, 203001 (2015).
[2] R. Schmidt and M. Lemeshko, Phys. Rev. X **6**, 011012 (2016).
[3] M. Lemeshko, Phys. Rev. Lett. **118**, 095301 (2017).
[4] Yu. Shchadilova, *"Viewpoint: A New Angle on Quantum Impurities"*, Physics **10**, 20 (2017).

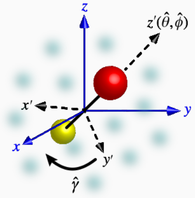
Backup slide # 3: canonical transformation

We apply a canonical transformation

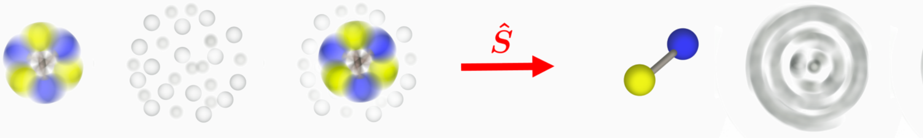
$$\boxed{\hat{S} = e^{-i\hat{\phi}\otimes\hat{\Lambda}_z} e^{-i\hat{\theta}\otimes\hat{\Lambda}_y} e^{-i\hat{\gamma}\otimes\hat{\Lambda}_z}}$$

where $\hat{\Lambda} = \sum_{\mu\nu} b^{\dagger}_{k\lambda\mu} \vec{\sigma}_{\mu\nu} b_{k\lambda\nu}$ 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