Molecular impurities interacting with a many-body environment: dynamics in Helium nanodroplets

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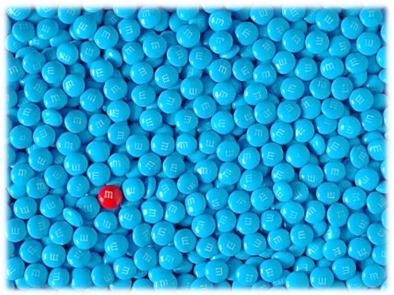
Definition: one (or a few particles) interacting with a many-body environment.

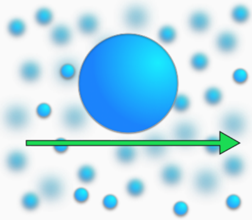
How are the properties of the particle modified by the interaction?

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



From impurities to quasiparticles

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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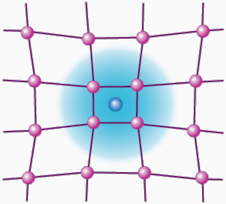

Image from: F. Chevy, Physics **9**, 86.

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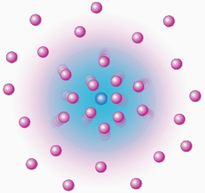

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Structureless impurity: translational
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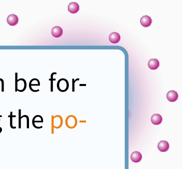
This scenario (with a bosonic bath) can be formalized in terms of quasiparticles using the polaron and the Fröhlich Hamiltonian.



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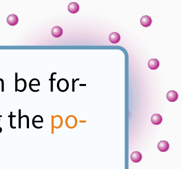

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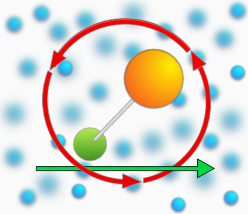

Composite impurity: translational *and internal* (i.e. rotational) degrees of freedom/linear and angular momentum exchange.

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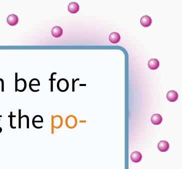

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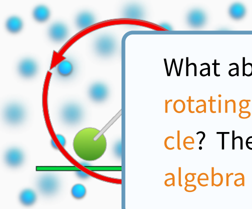


nd internal near and

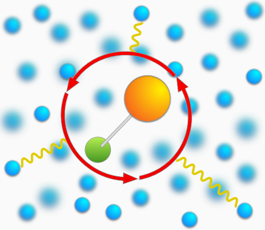
What about a rotating particle? Can there be a rotating counterpart of the polaron quasiparticle? The main difficulty: the non-Abelian SO(3) algebra describing rotations.

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).
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$\lambda = 0$: spherically symmetric part.
$\lambda \geq 1$ anisotropic part.

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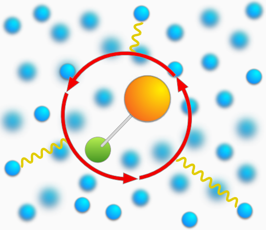

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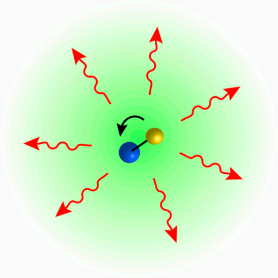
Composite impurities: where to find them

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

- Ultracold molecules and ions.



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

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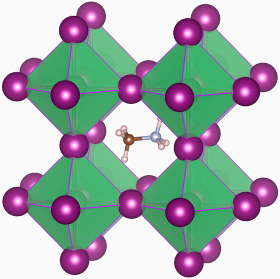

T. Chen et al., PNAS **114**, 7519 (2017).
J. Lahnsteiner et al., Phys. Rev. B **94**, 214114 (2016).
Image from: C. Eames et al, Nat. Comm. **6**, 7497 (2015).

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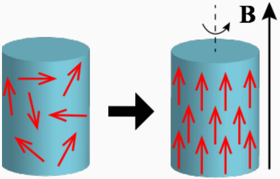

J.H. Mentink, M.I. Katsnelson, M. Lemeshko, *"Quantum many-body dynamics of the Einstein-de Haas effect"*, arXiv:1802.01638

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- Angular momentum transfer from the electrons to a crystal lattice.
- Molecules embedded into helium nanodroplets.

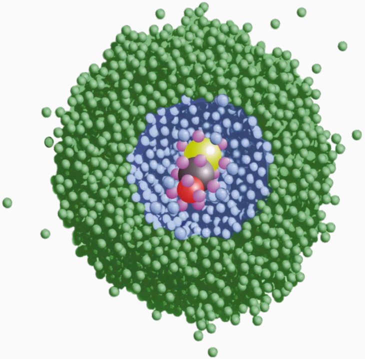
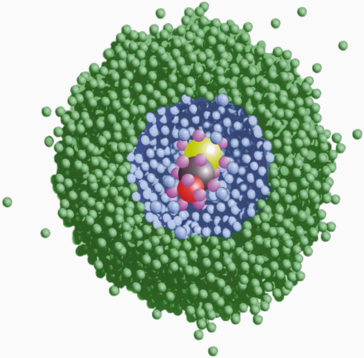


Image from: J. P. Toennies and A. F. Vilesov, Angew. Chem. Int. Ed. **43**, 2622 (2004).

Out-of-equilibrium dynamics of molecules in He nanodroplets

Molecules embedded into helium nanodroplets:



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Dynamical alignment of molecules in He nanodroplets

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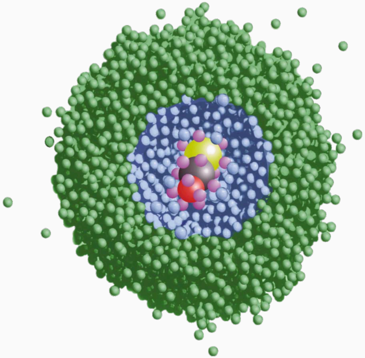

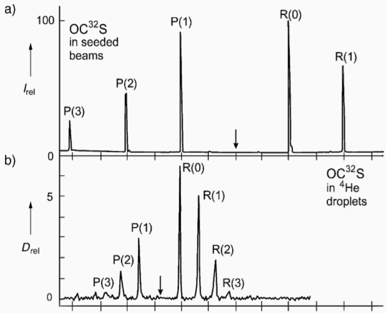

Gas phase (free)

in ^{4}He

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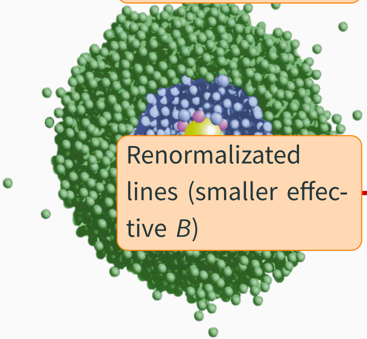
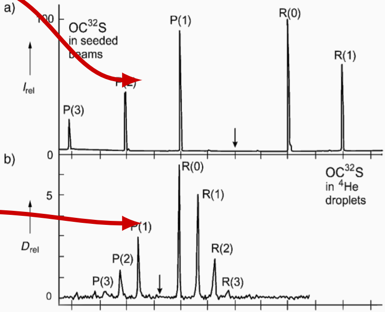
Molecules embedded into helium nanodroplets:

Rotational spectrum



Renormalizated lines (smaller effective *B*)



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Dynamical alignment of molecules in He nanodroplets

Dynamical alignment experiments:

- 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:

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

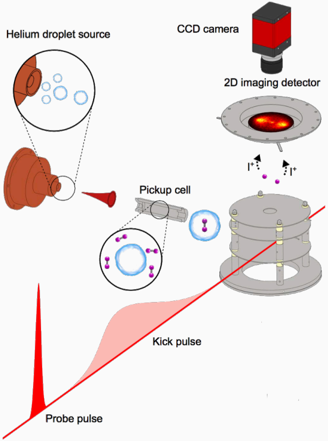


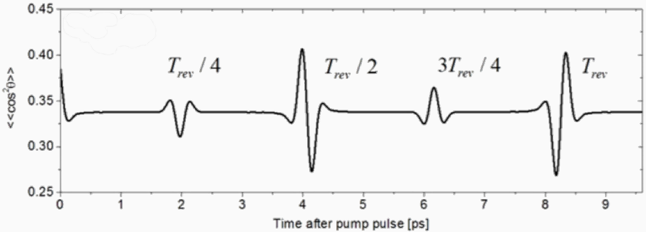
Image from B. Shepperson et al., Phys. Rev. Lett. **118**, 203203 (2017).

Dynamical alignment of molecules in He nanodroplets

Interaction of a free molecule with an off-resonant laser pulse

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

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:

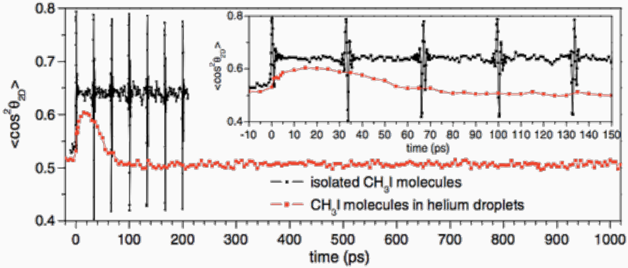


G. Kaya, Appl. Phys. B **6**, 122 (2016).

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).

Not even a qualitative understanding. Monte Carlo?

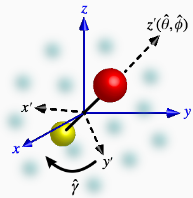
— Strong coupling
— Out-of-equilibrium dynamics
— Finite temperature ($B \sim k_B T$)

Canonical transformation

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

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

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



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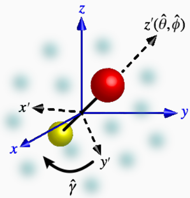

The $\hat{S}$ transformation takes us to the molecular frame.

- Macroscopic deformation of the bath, exciting an infinite number of bosons (cf. Lee-Low-Pines for the polaron).
- Simplifies angular momentum algebra.
- Hamiltonian diagonalizable through a coherent state transformation in the $B \to 0$ limit. An expansion in bath excitations is a strong coupling expansion.

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

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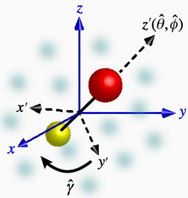

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Th… $\hat{S}$ transformation takes us to the …r frame.

✓ Strong coupling

— Out-of-equilibrium dynamics

— Finite temperature $(B \sim k_B T)$

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Dynamics: time-dependent variational Ansatz

We use a time-dependent variational Ansatz:

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

Lagrangian on the variational manifold defined by $|\psi\rangle$:

$$\mathcal{L}_{T=0} = \langle\psi|\mathrm{i}\partial_t - \hat{\mathcal{H}}|\psi\rangle$$

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 $x_i = \{g_{LM}, \alpha_{k\lambda n}\}$.

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

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— Finite temperature ($B \sim k_B T$)

Finite-temperature dynamics

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

For the bath: defining the 'Chevy operator'

$$\hat{O} = g_{LM}(t) \left| LM0 \right\rangle \mathbb{1} + \sum_{k\lambda n} \alpha^{LM}_{k\lambda n}(t) \left| LMn \right\rangle \hat{b}^\dagger_{k\lambda n}$$

at $T = 0$ the Lagrangian is

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

suggesting that at finite temperature

$$\mathcal{L}_T = \mathrm{Tr}\left[\rho_0 \, \hat{O}^\dagger (\mathrm{i}\partial_t - \hat{\mathcal{H}}) \hat{O} \right]$$

where ρ_0 is the density matrix for the medium.

[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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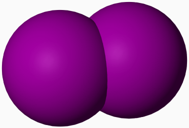
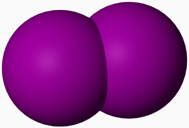
Theory vs. experiments: I_2



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



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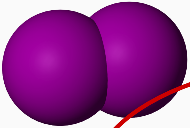
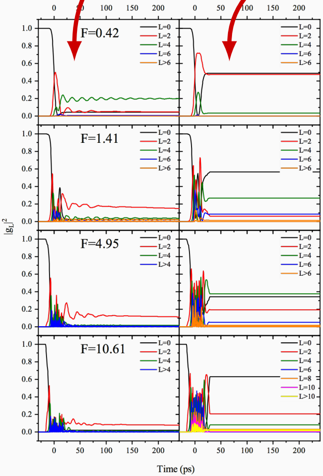
Which rotational states are populated as the laser is switched on, and after?



Comparison of the theory with preliminary experiment… dt group, Aarhus University, … s: I_2.

In Helium

Free molecule

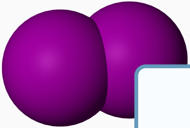


Which rotational states are populated as the laser is switched on, and after?

Free case: the angular momentum goes to the molecule.

In a Helium droplet: the angular momentum goes to the molecule *and* to the bath.

Theory vs. experiments: I_2



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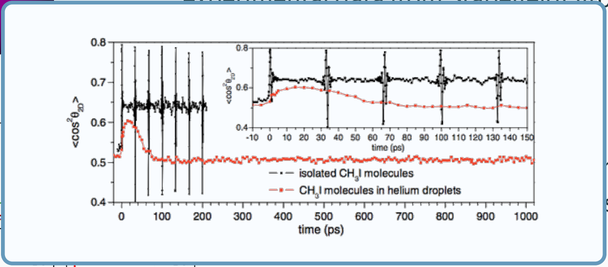
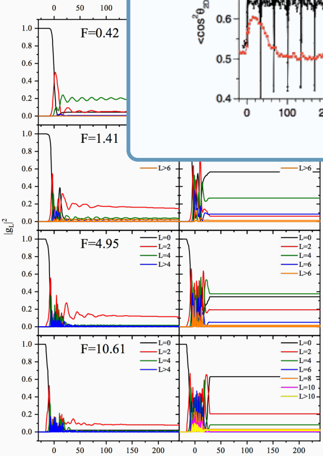


re

switched



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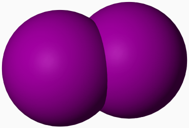
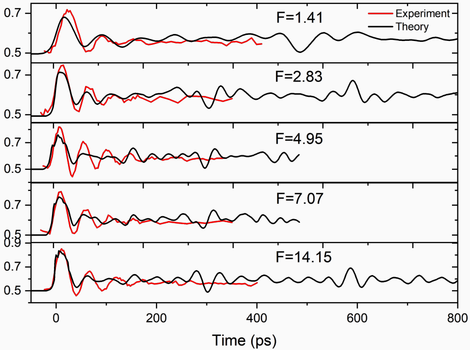
In a Helium droplet: the angular momentum goes to the molecule *and* to the bath.

Theory vs. experiments: I_2



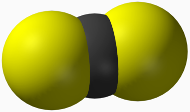
Comparison of the theory with preliminary experimental data from Stapelfeldt group, Aarhus University, for different molecules: I_2.



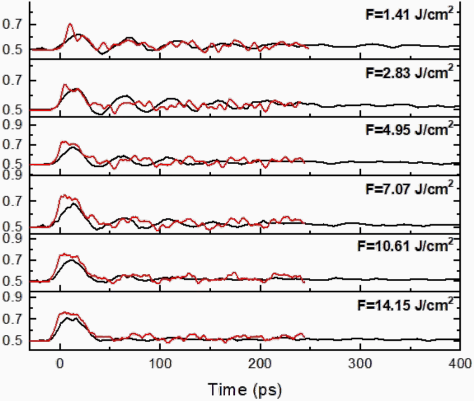
$\left\langle \cos^2 \hat{\theta}_{2D} \right\rangle (t)$

Laser fluence F measured in J/cm^2

Theory vs. experiments: CS_2

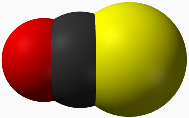


Comparison of the theory with preliminary experimental data from Stapelfeldt group, Aarhus University, for different molecules: CS_2.

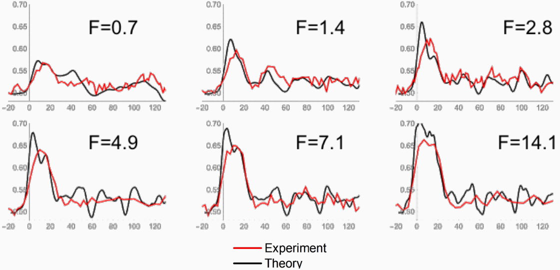


$$\left\langle \cos^2 \hat{\theta}_{2D} \right\rangle (t)$$

Theory vs. experiments: *OCS*



Comparison of the theory with preliminary experimental data from Stapelfeldt group, Aarhus University, for different molecules: *OCS*.

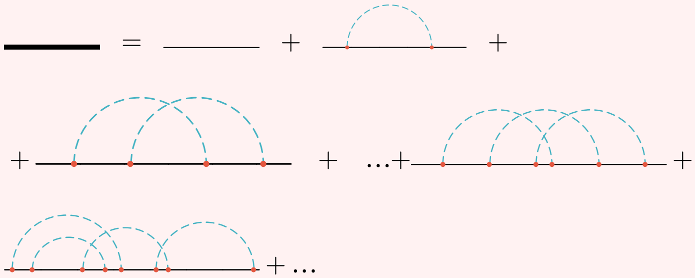


$\left\langle \cos^2 \hat{\theta}_{2D} \right\rangle (t)$

Laser fluence F measured in J/cm^2, time measured in *ps*.

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 looks like?

Connecting DiagMC and the theory of molecular simulations!

GB and M. Lemeshko, Phys. Rev. B **96**, 419 (2017).
GB, T.V. Tscherbul, M. Lemeshko, arXiv:1803:07990

Conclusions

- The angulon quasiparticle: a quantum rotor dressed by a field of many-body excitations.
- Canonical transformation and finite-temperature variational Ansatz.
- Out-of-equilibrium dynamics of molecules in He nanodroplets can be interpreted in terms of angulons.

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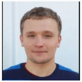
Lemeshko group @ IST Austria:

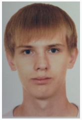


Misha Lemeshko

Dynamics in He

Enderalp Yakaboylu

Xiang Li



Igor Cherepanov

Wojciech Rządkowski

Collaborators:

Dynamical alignment experiments

Henrik Stapelfeldt (Aarhus)

Thank you for your attention.

Der Wissenschaftsfonds.

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Backup slide # 1

Free rotor propagator

$$G_{0,\lambda}(E) = \frac{1}{E - B\lambda(\lambda+1) + \mathrm{i}\delta}$$

Interaction propagator

$$\chi_\lambda(E) = \sum_k \frac{|U_\lambda(k)|^2}{E - \omega_k + \mathrm{i}\delta}$$

Backup slide # 2

Backup slide # 3