n-dimensional Wave Packet Dynamics and Comparison with Approximate Methods

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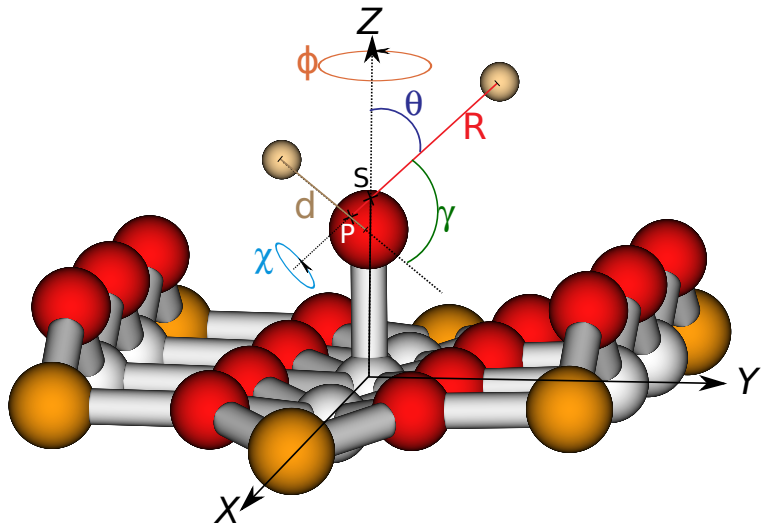
Wave Packet Dynamics on Semiconductor Surfaces

Research fields

- Photocatalytic reactions on Semiconductor Surfaces
  - Cluster models
  - Periodic calculations
  - CAS calculations for excited states
  - Wave packet dynamics
  - Open quantum systems

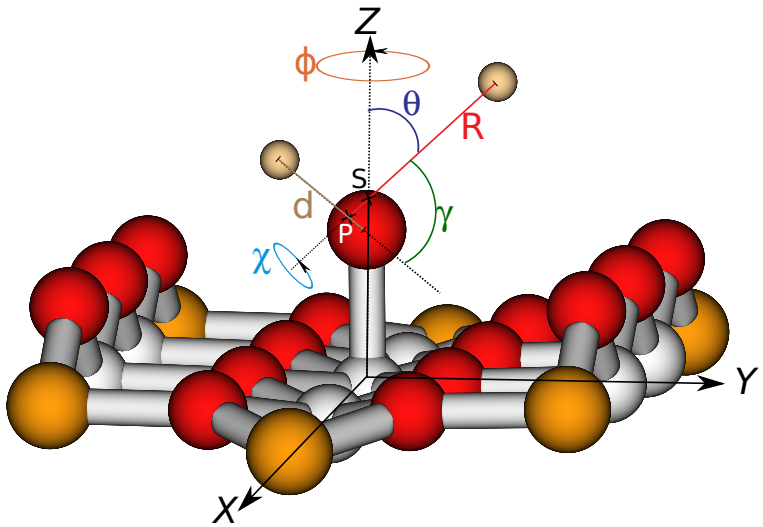


[0] J. Mitschker, T. Klüner, *Phys. Chem. Chem. Phys.* **2015**, 17, 268.

Theory

Time-independend Schrödinger equation:

$$\hat{H}\Psi(x) = E\Psi(x)$$



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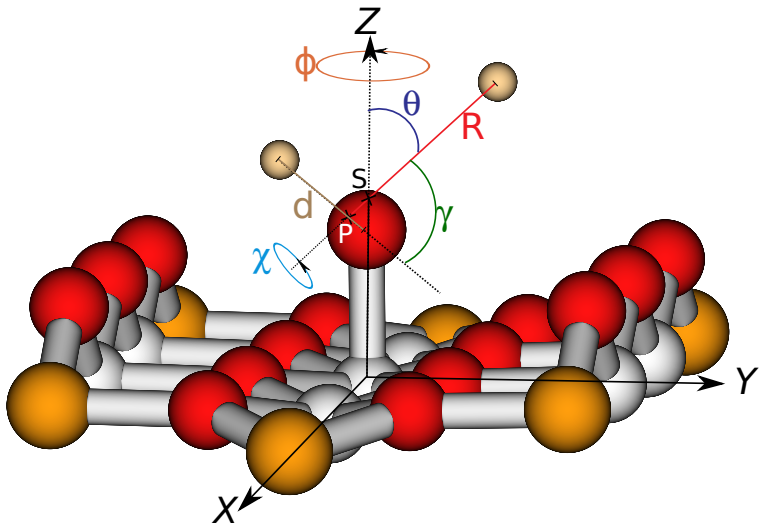
Born-Oppenheimer approximation



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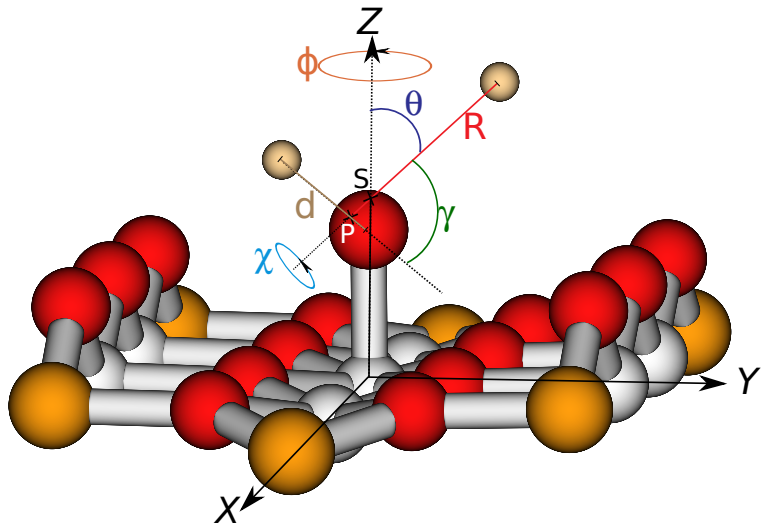
$\rightarrow$ Electronic Schrödinger equation

$$\hat{H}_{el}\Psi_{el}(x) = E_{el}\Psi_{el}(x)$$



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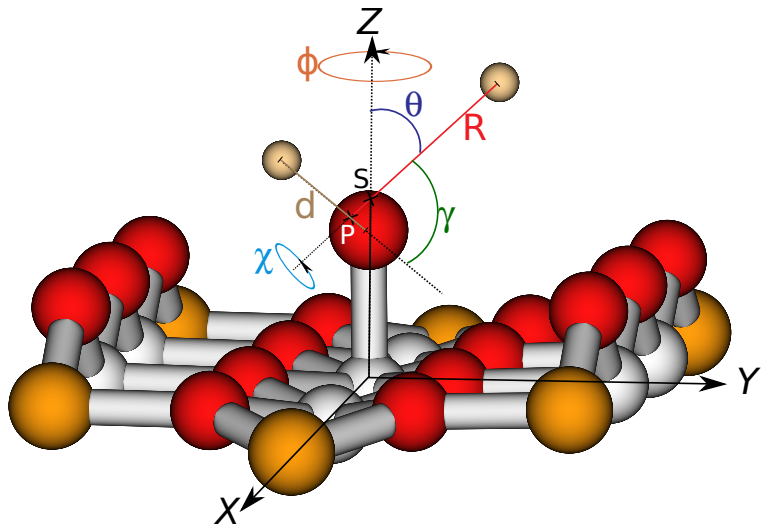

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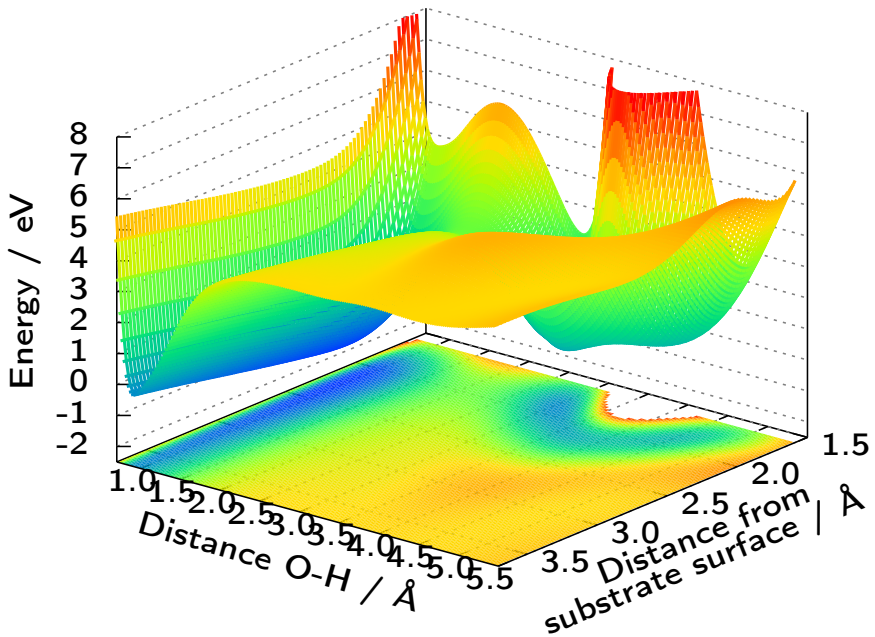
Potential Energy Surface (PES)



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Potential Energy Surface (PES)
Wavepacket Dynamics on the PES:

$$i\frac{\partial}{\partial t}\Psi_{Nuc}(x,t) = \hat{H}_{Nuc}\Psi_{Nuc}(x,t)$$

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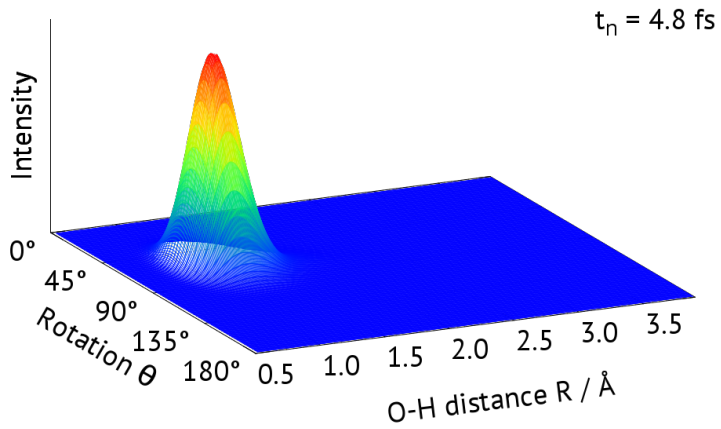

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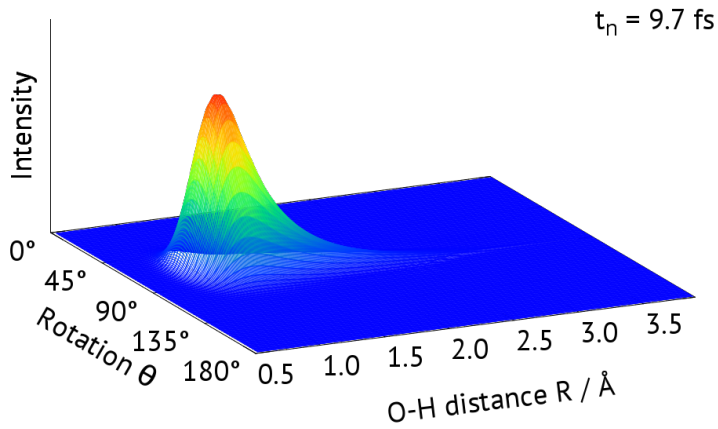

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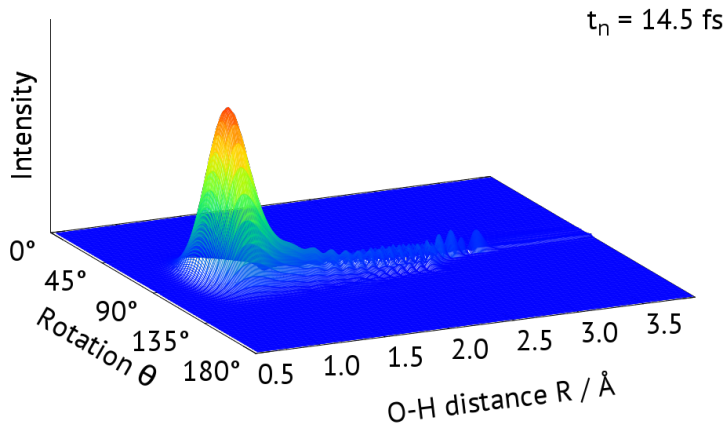

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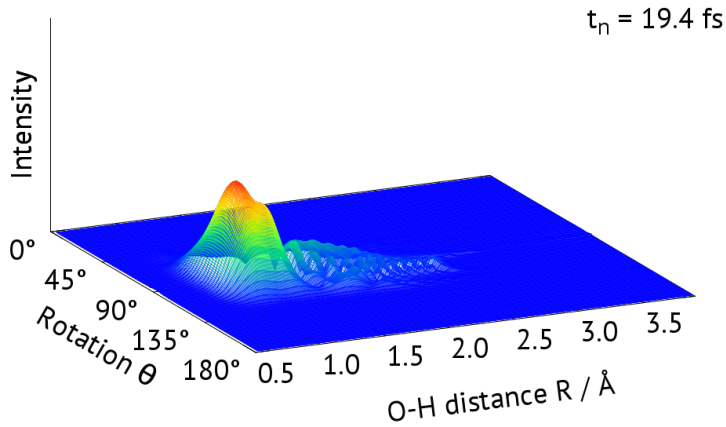

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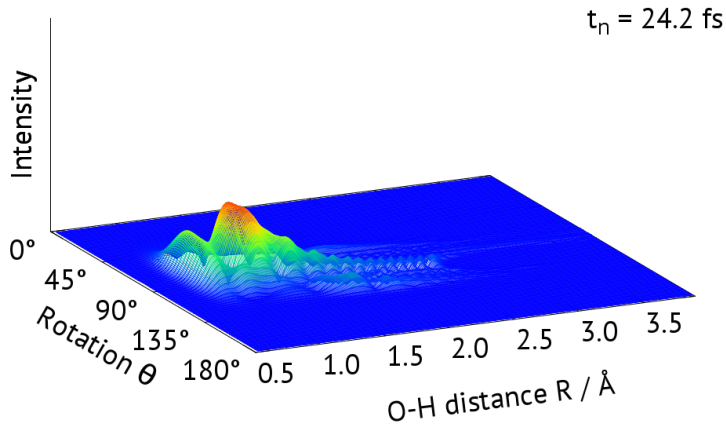
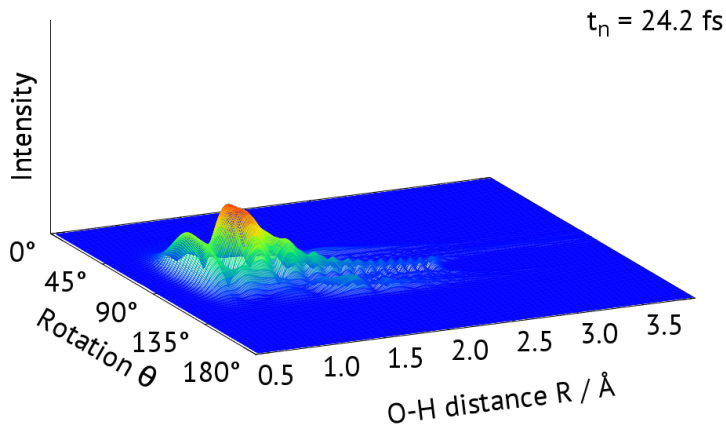
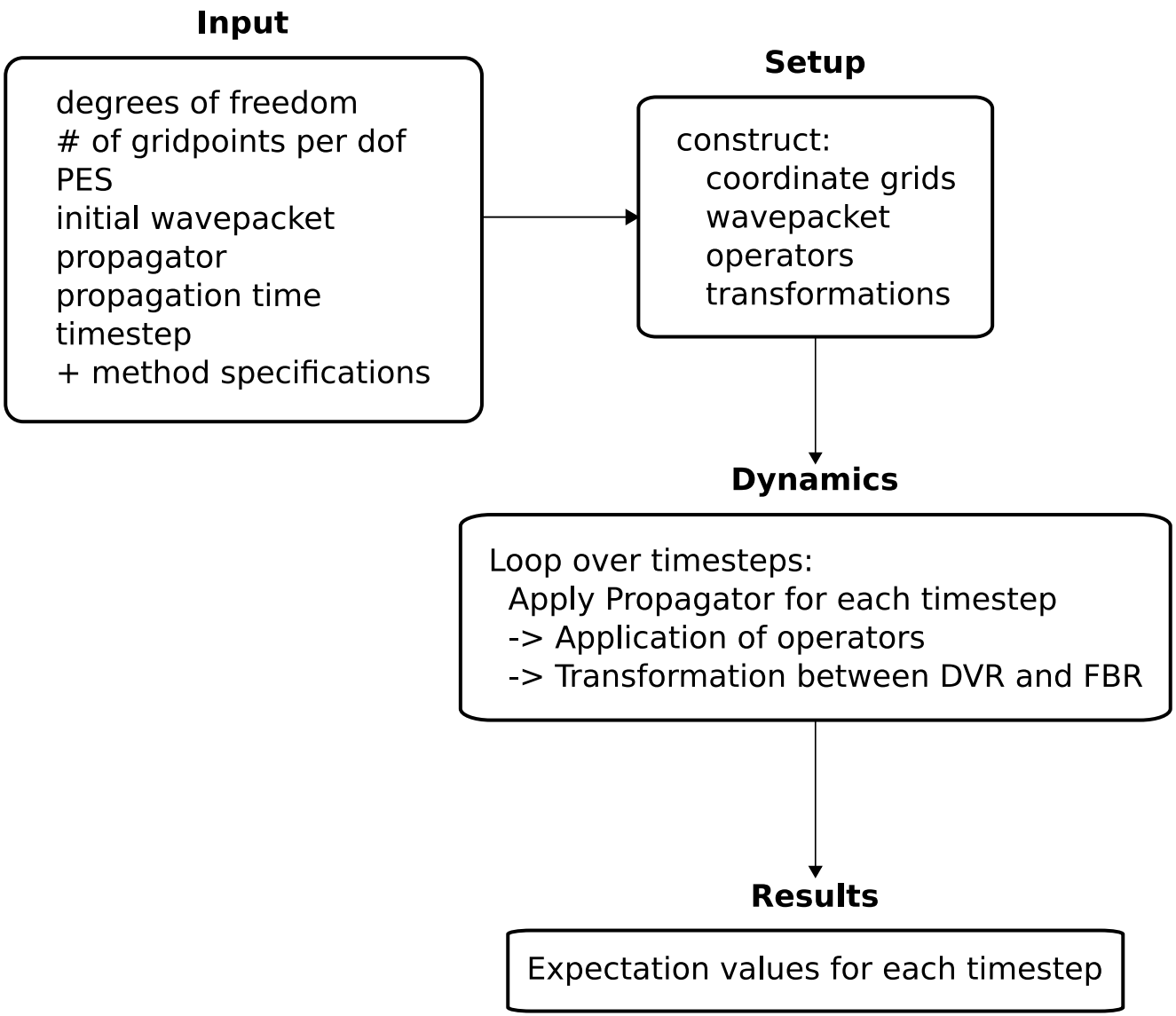


Results

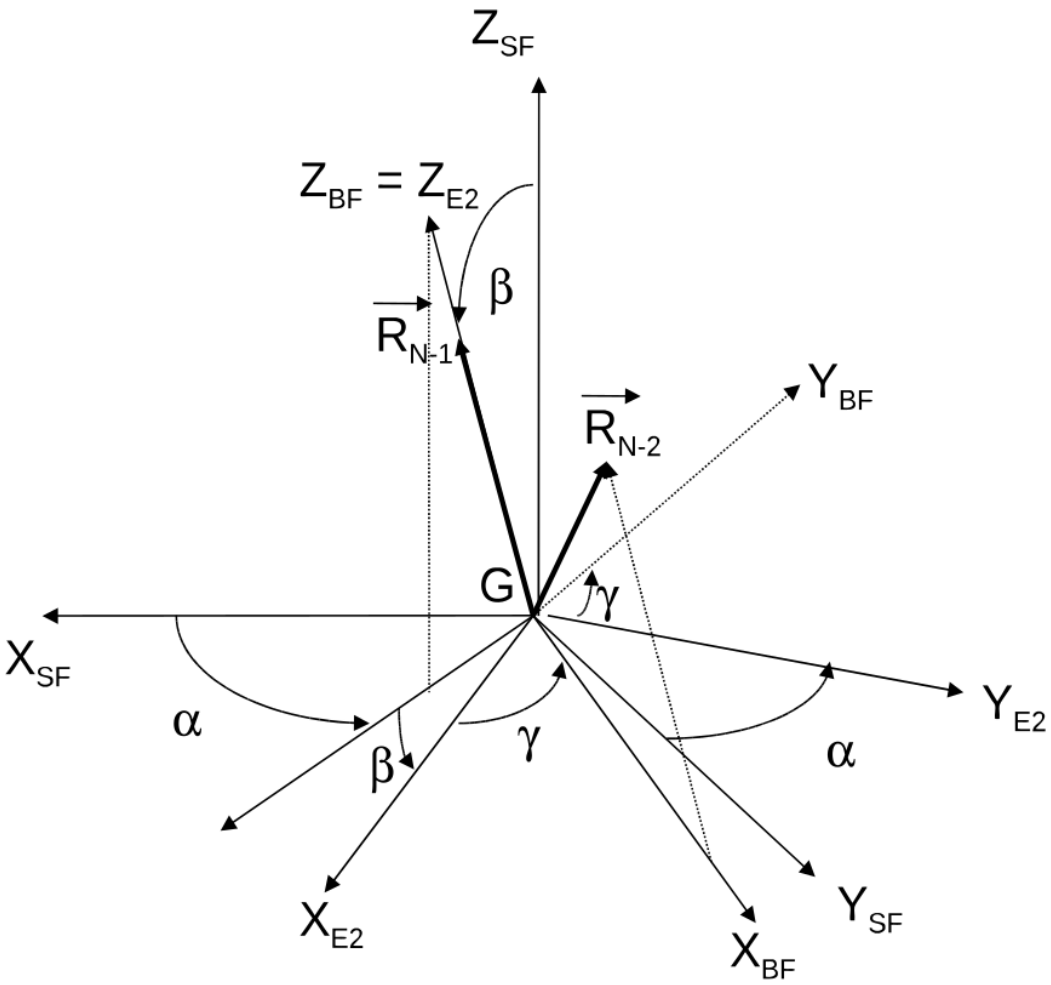
Expectation values:

- Desorption probability
- Dissociation probability
- Position
- Momentum
- Kinetic energy
- Potential energy
- ...




Input
degrees of freedom
# of gridpoints per dof
PES
initial wavepacket
propagator
propagation time
timestep
+ method specifications
Setup
construct:
coordinate grids
wavepacket
operators
transformations
Dynamics
Loop over timesteps:
Apply Propagator for each timestep
-> Application of operators
-> Transformation between DVR and FBR
Results
Expectation values for each timestep

n-dimensional Coordinates



Polyspherical Coordinates - Euler angles[1]

[1] F. Gatti, C. Iung *Physics Reports* 484, **2009**, 1–69.

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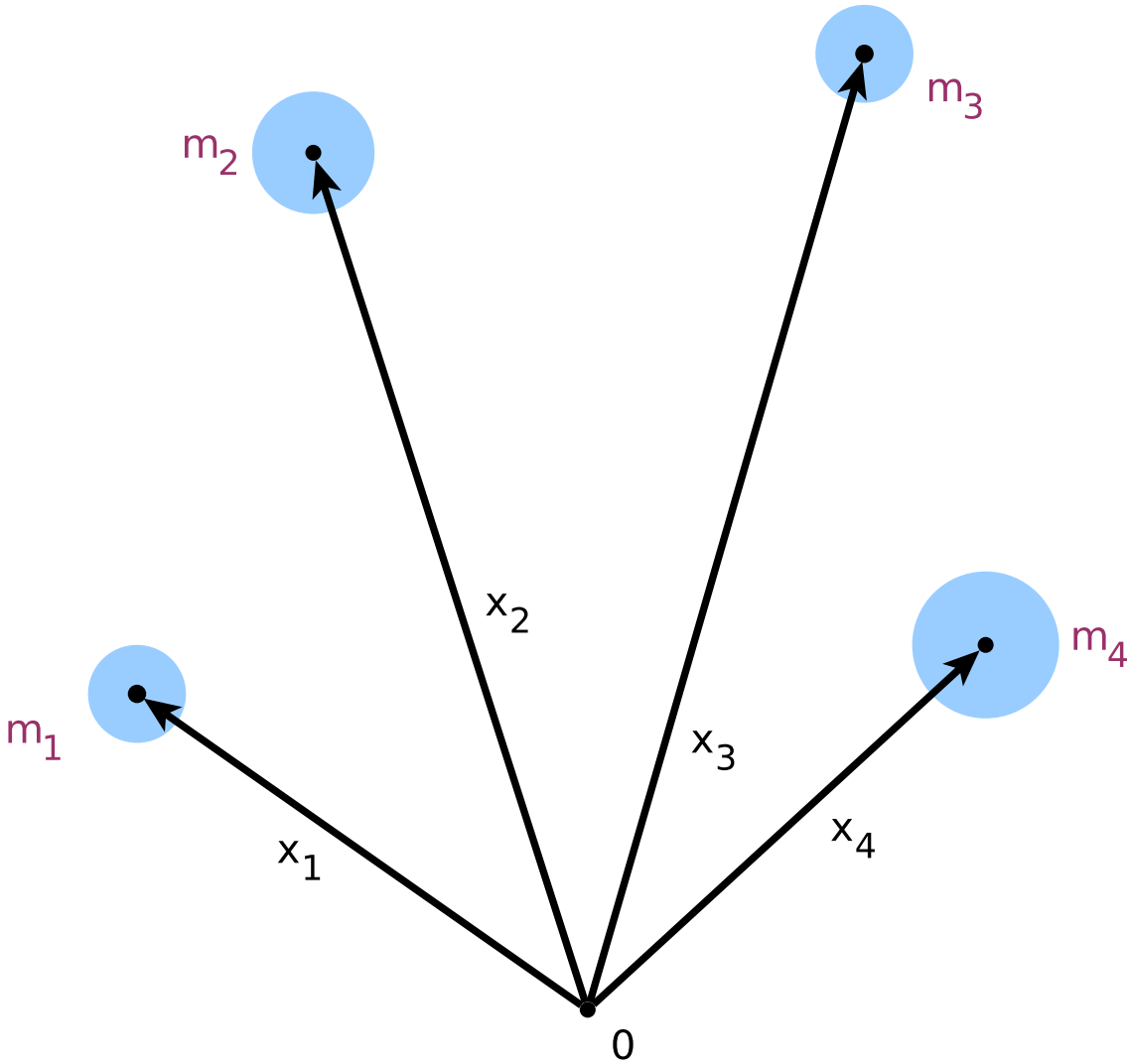

Jacobi vectors[2]

[2] https://commons.wikimedia.org/w/index.php?curid=32937580

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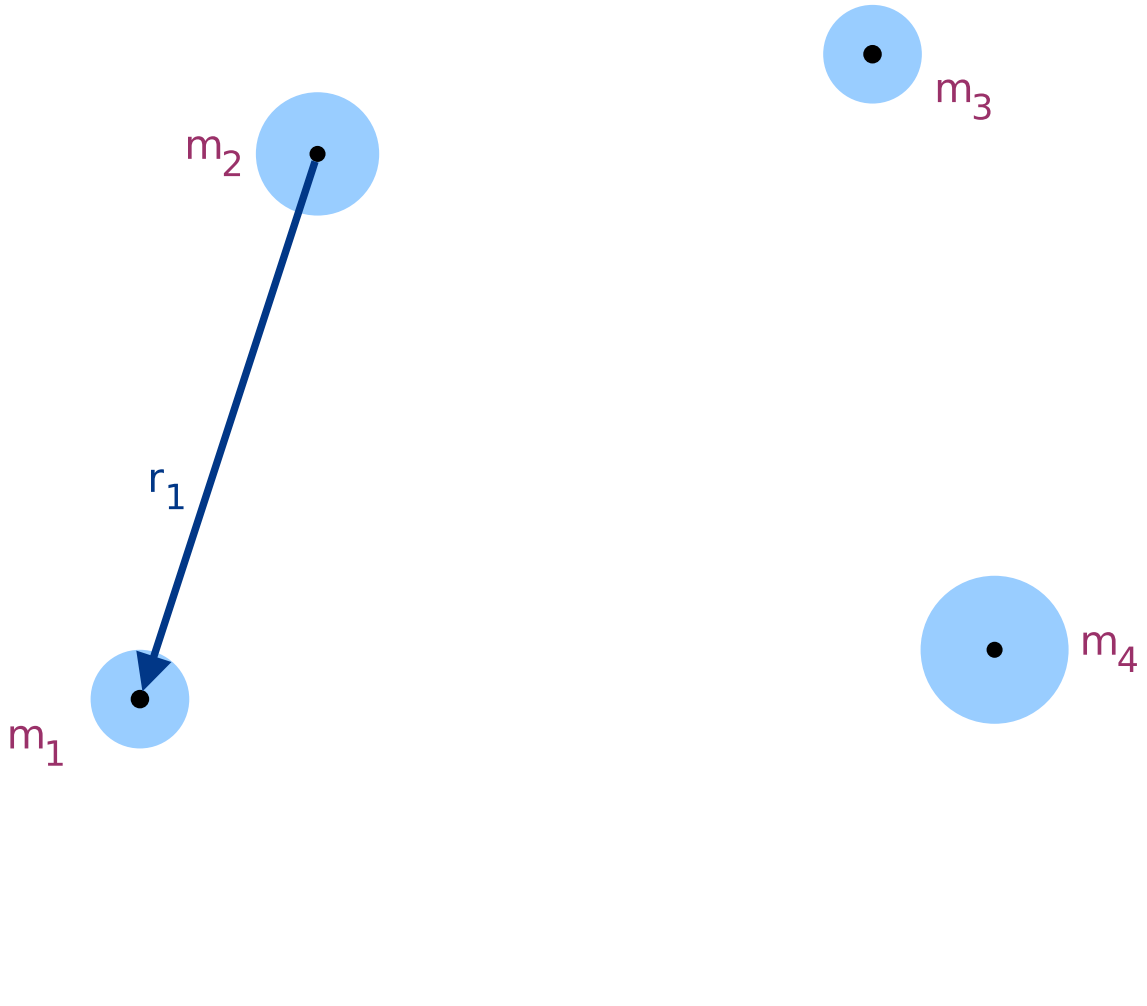

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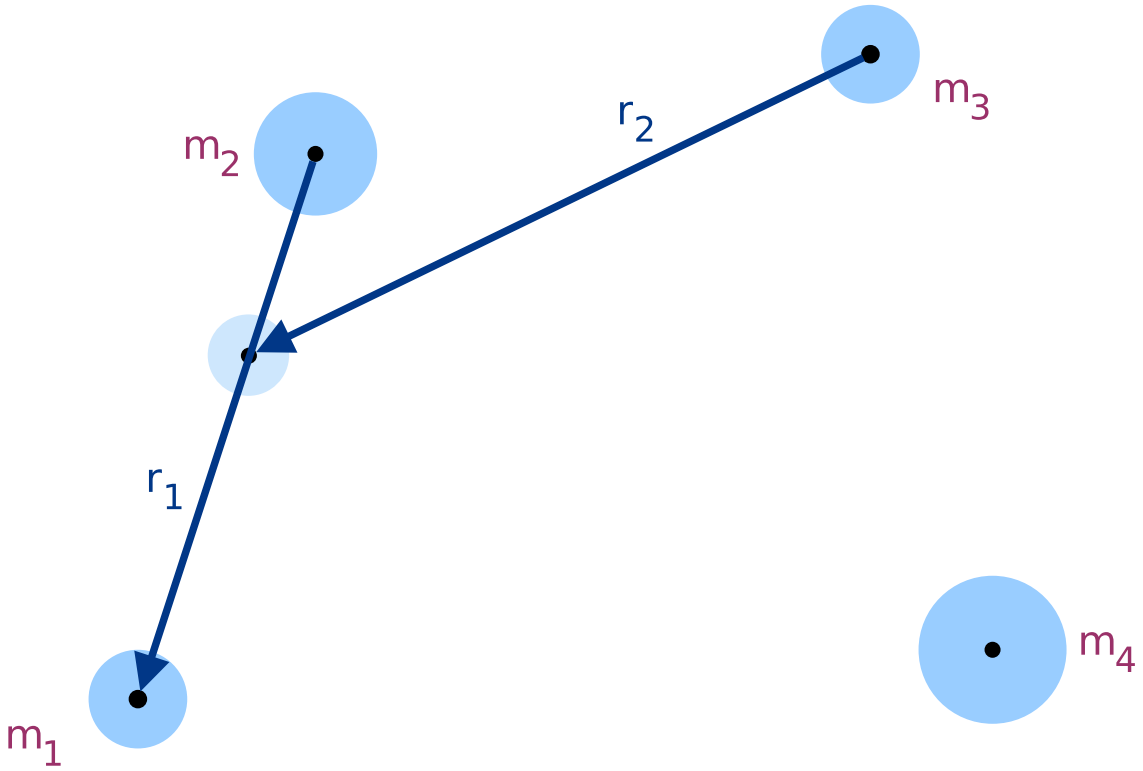

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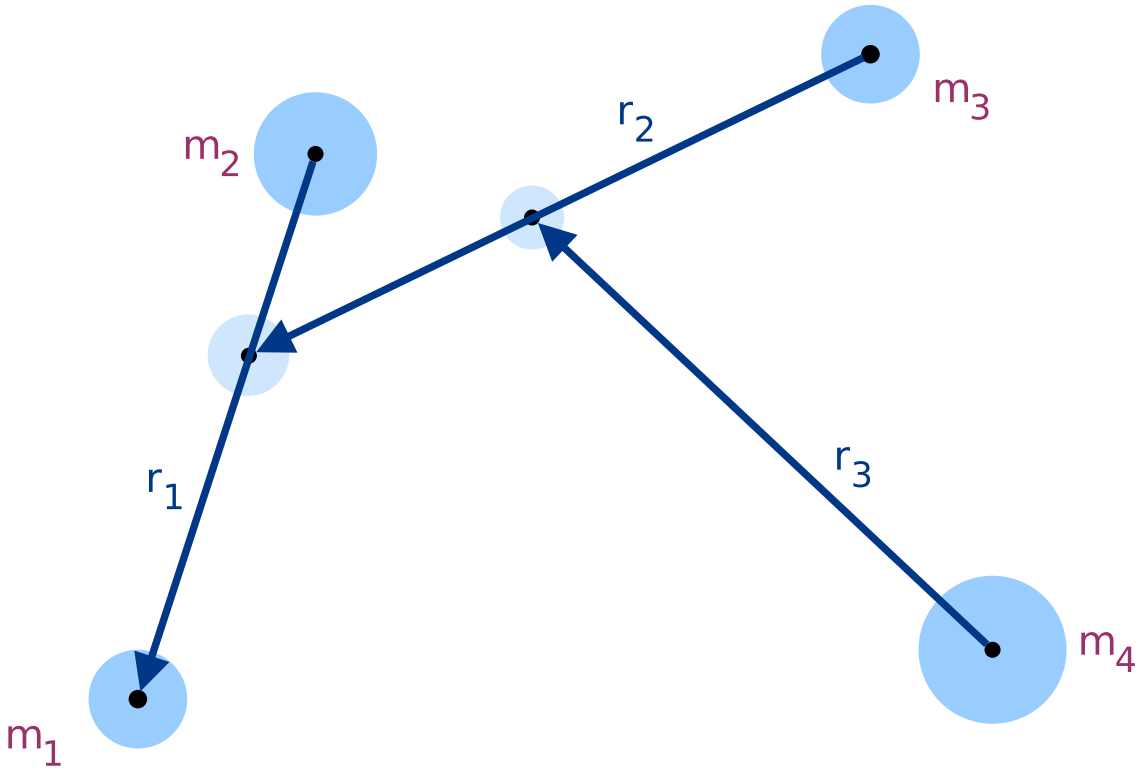

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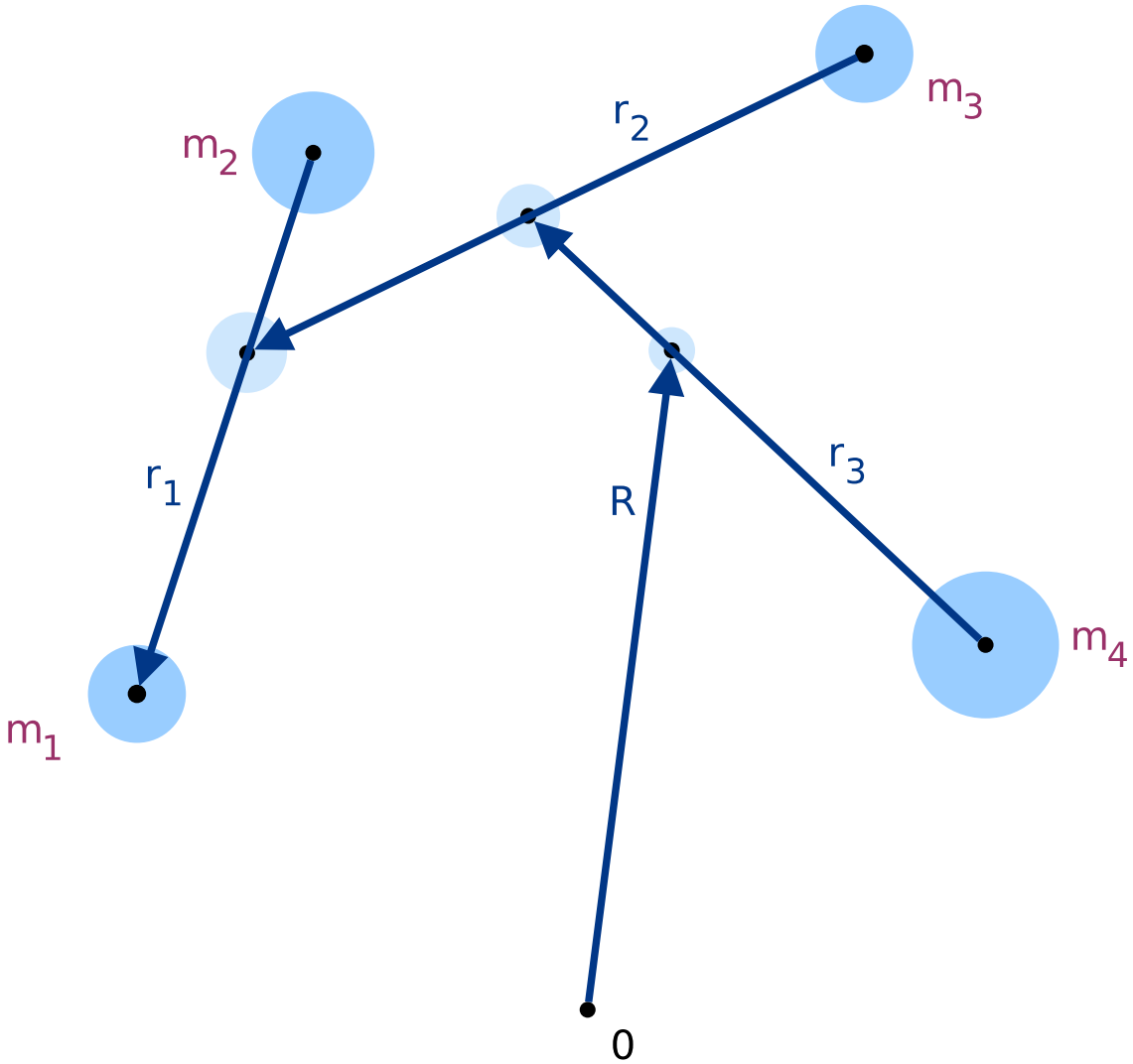

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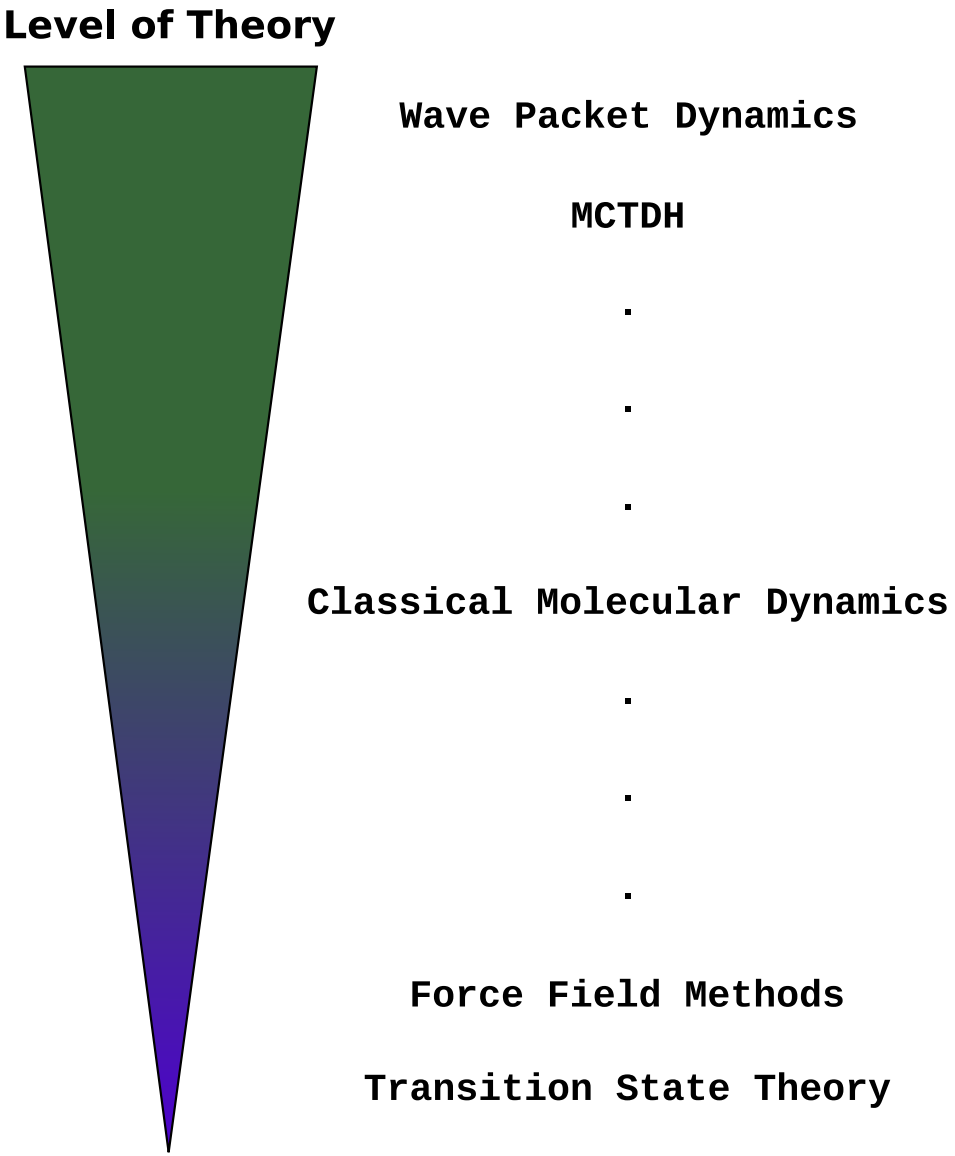
Comparison


Level of Theory
Wave Packet Dynamics
MCTDH
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.
.
Classical Molecular Dynamics
.
.
.
Force Field Methods
Transition State Theory

Thank you for your attention

Workgroup Klüner - Theoretical Chemistry