# *e*FMD: Fermionic Molecular Dynamics for electronic structure theory.

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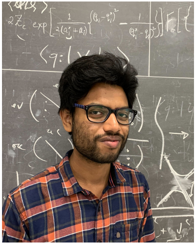
WATOC2020
Vancouver, BC, Canada
Jul 5, 2022

# Who?



Vivek Das (QuNB)

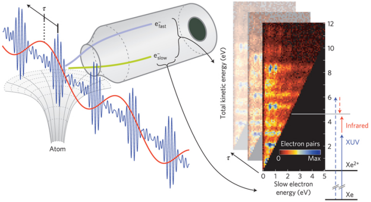
Anthony Balchin (University of Surrey)

Chris Cousins

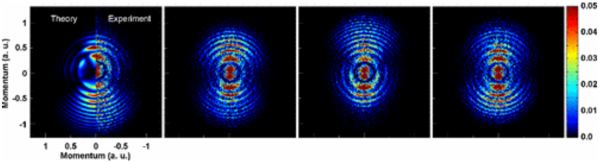
# Attosecond chemistry

## Attosecond

- X/UV pulse trains at $\Delta t \sim 10^{-16}$s
- Within Born-Oppenheimer




E. P. Manson et. al. (2014), Nat. Phys. 10, 207



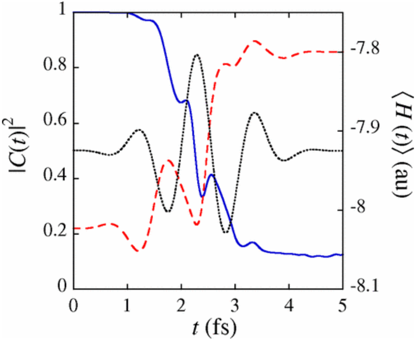

J. Mauritsson (2008), Phys. Rev. Lett. 100, 073003

# Time Dependent Schrödinger equation

- Time-dependent expansion

$$|\psi(t)\rangle = \sum_{\alpha \in \text{PES}} c_\alpha(t)|\Psi_\alpha\rangle$$

- ground + excited states




F Remacle, M Nest & R D Levine (2007) Phys. Rev. Lett. 99, 183902

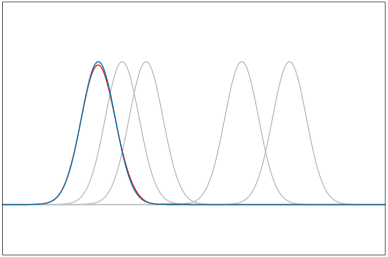
# Free particle

- Exact Gaussian

$$|\psi(x,t)|^2 = \frac{e^{-\frac{(x-vt)^2}{1+t^2}}}{\sqrt{\pi(1+t^2)}}$$

- Approximate in finite basis

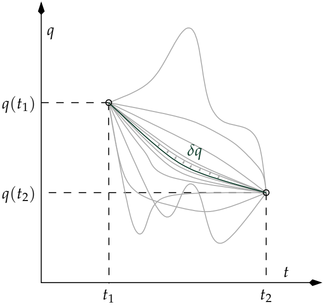
$$|\psi(x,t)|^2 = \left|\sum_n c_n(t)\phi_n(x)\right|^2$$



# Time Dependent Variational Principe (TDVP)

## Stationary Action

$$\mathcal{S} = \int_{t_1}^{t_2} \langle \psi[q] | i\hbar \frac{\partial}{\partial t} - H | \psi[q] \rangle dt$$




- Euler-Lagrange equations

$$i\hbar \sum_k C_{ik} \dot{q}_k = \frac{\partial \langle H \rangle}{\partial q_i^*}$$

- Dynamical system
- Exact in full Hilbert space

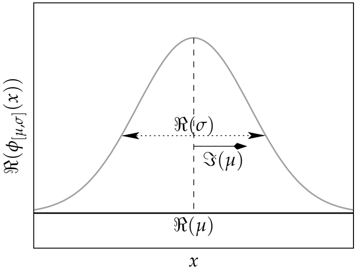
$\rightarrow$ Approximations

# Fermionic Molecular Dynamics (FMD)

$$|\psi[q]\rangle = \begin{vmatrix} e^{-\frac{(\vec{r}_1-\vec{\mu}_1)^2}{2\sigma_1^2}} & \dots & e^{-\frac{(\vec{r}_1-\vec{\mu}_N)^2}{2\sigma_N^2}} \\ \vdots & \ddots & \vdots \\ e^{-\frac{(\vec{r}_N-\vec{\mu}_1)^2}{2\sigma_1^2}} & \dots & e^{-\frac{(\vec{r}_N-\vec{\mu}_N)^2}{2\sigma_N^2}} \end{vmatrix}$$

- Nuclear structure physics
- Slater Determinant of Gaussians
- Semi-classical interpretation

$$\mu(t) = \langle \hat{x}(t) \rangle - \frac{i\sigma(t)}{\hbar} \langle \hat{p}(t) \rangle$$

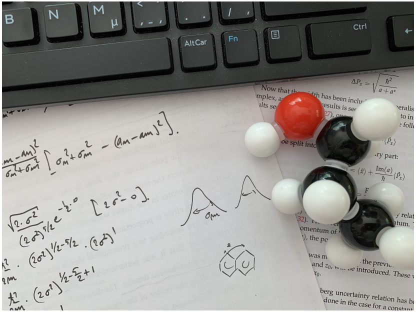



H Feldmeier & T. Neff (2017) Nuclear Particle Correlations and Cluster Physics

# Electronic Structure theory

## project timeline

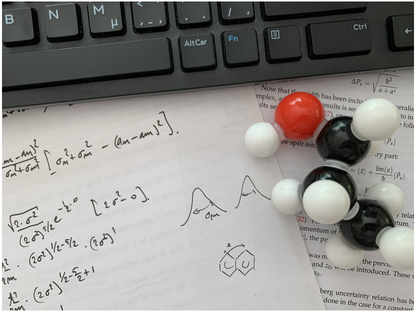
- Heisenberg ($1e^-$)
- Pauli ($Ne^-$)
- $t$-dependent interactions
- Correlation



# Electronic Structure theory

## project timeline

- Heisenberg ($1e^-$)



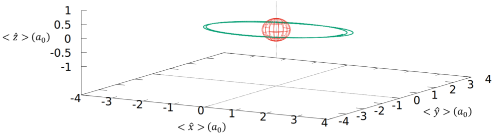
# Test case 1: H

## hydrogen

- "Kepler" orbits

Observables

$$\langle\vec{r}(t)\rangle = \langle\psi(t)|\vec{r}|\psi(t)\rangle$$
$$E(t) = \langle T(t)\rangle + \langle V(t)\rangle$$



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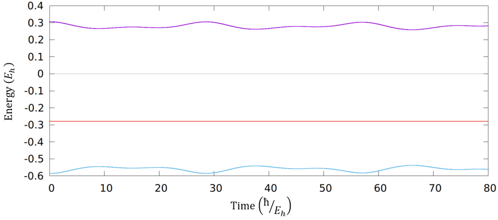

# Test case 1: H

## hydrogen

- Ionization

Observables

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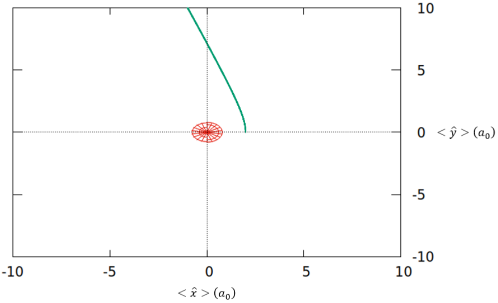

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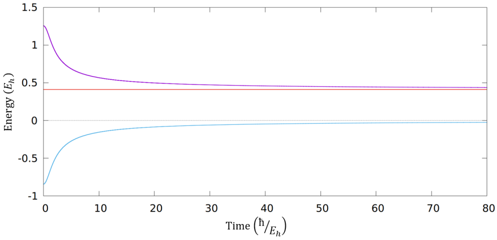

# Test case 1: H

## hydrogen

- Add damping

Observables

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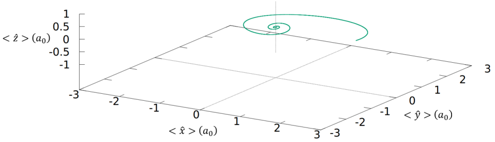

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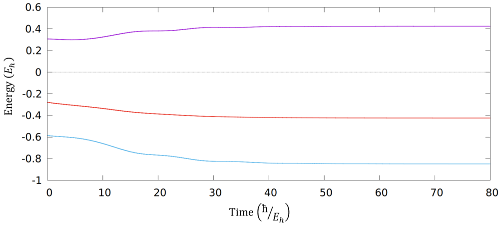


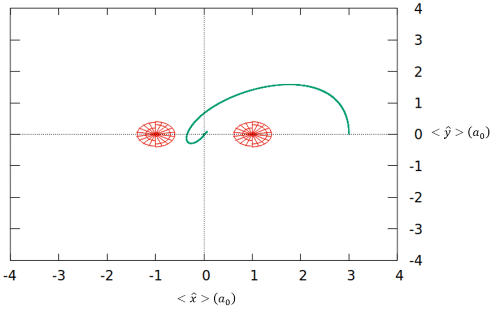
# Test case 2: $H_2^+$

## di-hydrogen cation

- Bonding orbitals

Observables

$$\langle \vec{r}(t) \rangle = \langle \psi(t) | \vec{r} | \psi(t) \rangle$$
$$E(t) = \langle T(t) \rangle + \langle V(t) \rangle$$



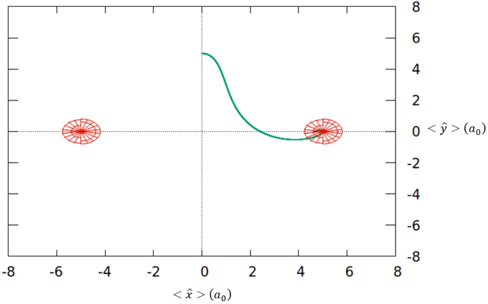
# Test case 2: $H_2^+$

## di-hydrogen cation

- Symmetry breaking

Observables

$$\langle \vec{r}(t) \rangle = \langle \psi(t) | \vec{r} | \psi(t) \rangle$$
$$E(t) = \langle T(t) \rangle + \langle V(t) \rangle$$



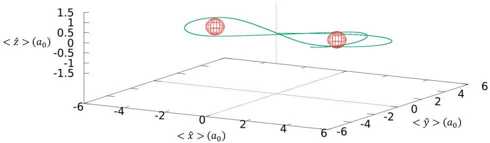
# Test case 2: $H_2^+$

## di-hydrogen cation

- others ...

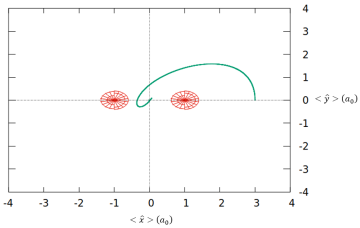
Observables

$$\langle \vec{r}(t) \rangle = \langle \psi(t) | \vec{r} | \psi(t) \rangle$$
$$E(t) = \langle T(t) \rangle + \langle V(t) \rangle$$



# Conclusions & Outlook

- $t$-Dependent Variational Principle
- $e^-$ Fermionic MD




thanks!