Real Time Dynamics of Electrons with Coupled Gaussian Wavepackets

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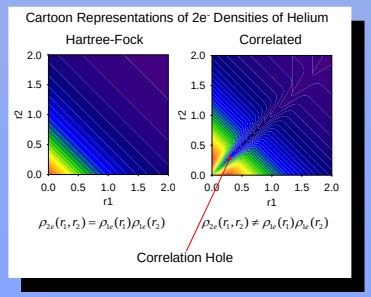
Electron Correlation in Atoms and Molecules

Traditional Treatments of Electron Correlation



- Ab Initio Method
  - Many electron wavefunction represented in a large basis of uncorrelated basis functions
  - Computationally Expensive
- Density Functional Theory (DFT)
  - Correlation energy added using knowledge of the electron gas as a starting point
  - No systematic method of improvement
  - Excited states are an open question

Coupled Frozen Gaussians Method

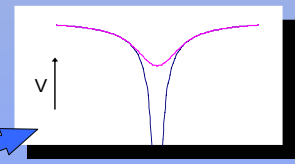
Why Coupled Frozen Gaussians?

- Classical trajectories are correlated
- Suppose we want a time-dependent basis which is classical-like in which to solve the Schrödinger equation
- Frozen Gaussians (aka Coherent States) are minimal uncertainty basis functions with a given average position and momentum

Classical Propagation

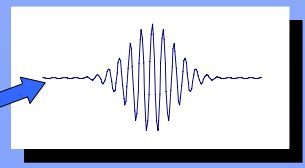
- R and P propagated according to classical equations of motion
- Classical potential is the mean field potential experience by the basis function

$$V_{classical}=\langle\chi|V|\chi\rangle$$



What is a Frozen Gaussians?

$$\chi_\gamma^K\left(\mathbf{R};\bar{\mathbf{R}}_\gamma^K(t),\bar{\mathbf{P}}_\gamma^K(t),\bar{\gamma}_\gamma^K(t),\boldsymbol{\alpha}_\gamma^K\right)=$$
$$=e^{\frac{i}{\hbar}\bar{\gamma}_\gamma^K(t)}\prod_{\rho=1}^{3N}\left(\frac{2\alpha_\rho^K}{\pi}\right)^{\frac{1}{4}}\exp\left[-\alpha_{r_\rho}^K\left(R_{r_\rho}-\bar{R}_{r_\rho}^K(t)\right)^2+i\bar{P}_{r_\rho}^K(t)\left(R_{r_\rho}-\bar{R}_{r_\rho}^K(t)\right)\right]$$



Time Info = Energy Info

- Propagate wavefunction

$$|\Psi(t)\rangle=e^{-iHt}|\Psi(0)\rangle$$

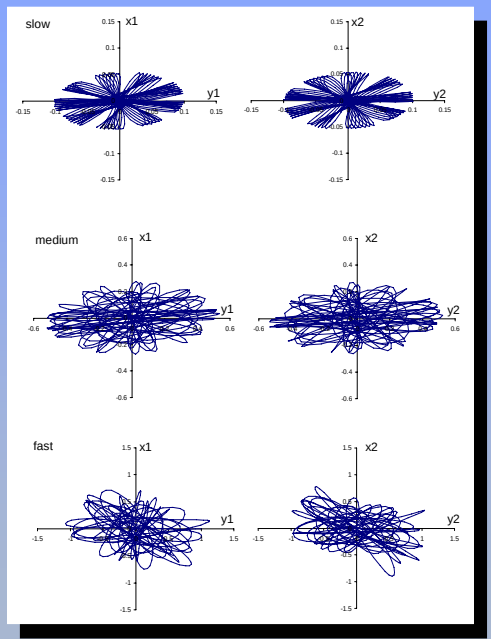
- Calculate Correlation Function

$$C(t)=\langle\Psi(0)|e^{-iHt}|\Psi(0)\rangle$$

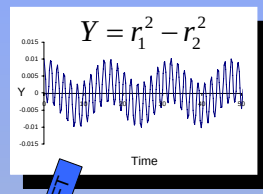
- Fourier Transform

$$C(\omega)=\int\langle\Psi(0)|e^{-iHt}|\Psi(0)\rangle e^{i\omega t}dt$$

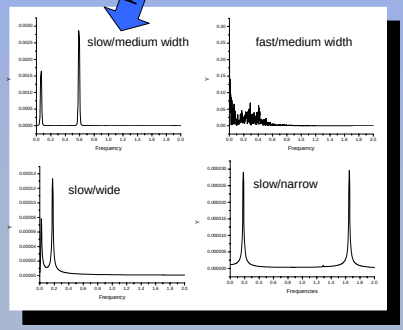
Classical Trajectories



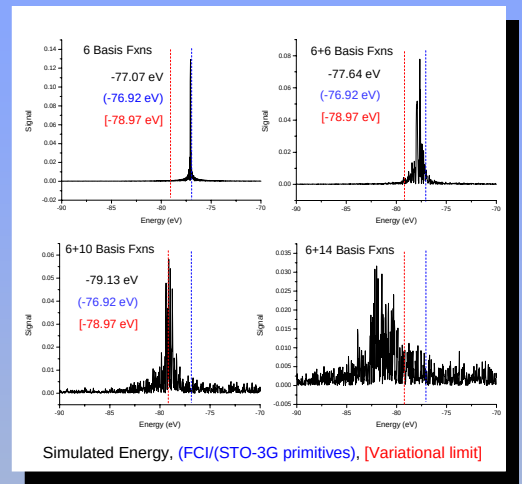
- Fast trajectories exhibit disordered behavior
- Fast trajectories have slower energy transfer between electrons
- Trajectory width effects energy transfer between electrons



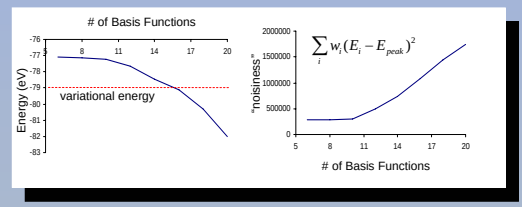
FT



Quantum Mechanical Results



Simulated Energy, (FCI/(STO-3G primitives), [Variational limit]



- We successful reproduce ab initio results with a small carefully chosen basis
- Choice of a larger basis leads to a noisy spectrum and a violation of the variational principle

Conclusions

- Coupled Frozen Gaussians offer the ability to include classical-like correlation in a quantum mechanical simulation. A new intuitive approach to the study of electron correlation my arise from such studies.
- Preliminary results of classical trajectory simulations suggest avenues for future study.
- Preliminary quantum mechanical results suggest numerical difficulties.

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