

# Nanoscale Structures & Devices

## Electronic Excitations – Time Dependent Density Functional Theory

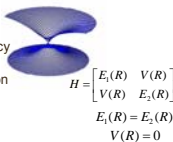
J. Coe, R. Haber, D. D. Johnson, B. Levine, R. M. Martin, T. J. Martinez, A. Toniolo, and I. Vasiliev  
Departments of Chemistry, Theoretical and Applied Mechanics, Materials Science and Engineering and Physics  
University of Illinois at Urbana-Champaign

### Overview

When electrons are excited, they are strongly affected by confinement in nanoscale systems, and often are strongly coupled to nuclear degrees of freedom. This forms the basis for many phenomena that control physical and chemical properties of materials such as optical spectra, photo-reactions and electronic transport. Applications to nanoscale systems could pave the way to new opto-electronic molecular devices. A major obstacle is the difficulty of accurately modeling electronically excited states, especially in large molecules and complex environments. Time dependent density functional theory (TDDFT) holds the promise to provide an accurate and computationally tractable method for modeling these excitations in complex systems.

**Conical Intersections (CIs)** are critical in excited state dynamics, serving as "funnels" which promote level crossing transitions.

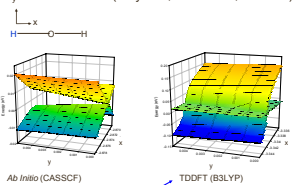
- Challenge for TDDFT
- Fundamental failure of present functionals
- Overall energetics predicted accurately
- Steps to improve the functionals



### Conical Intersections

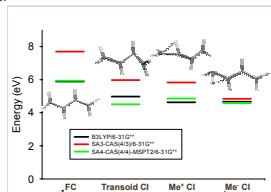
True electronic state degeneracy at one point which is lifted in at least two directions as a function of nuclear coordinates

**Example of water** — Other molecules are similar (ethylene, butadiene, stilbene)



**Fundamental error in TDDFT** — degenerate along an entire line. It can be shown analytically that the degeneracy should be a single point in this case. All local, gradient-corrected, and hybrid functionals we have tested show the same behavior (e.g. LDA, BLYP, PBE, PW91)

**Triumph in TDDFT** — Intersection energies for butadiene agree well with expensive SA4-CAS(4/4)-MSPT2 calculations — more accurate than state-averaged CASSCF, a multi-reference method often used for excited states.

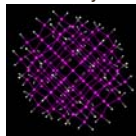


Vertical excitation energy in excellent agreement with CASPT2 and experiment.

CI geometries determined using TDDFT, CASPT2, and CASSCF. TDDFT predicts the existence of these points correctly and also predicts their energies accurately.

### Optical Properties of Semiconductor Nanoclusters – collaboration with J. R. Chelikowsky

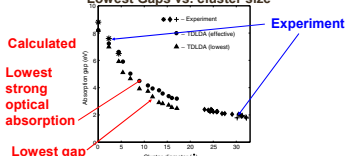
**Example of cluster saturated with H:**



### TDDFT calculations with the local LDA approximation

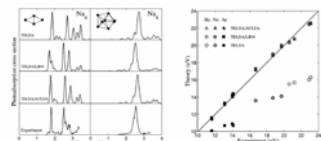
**Increased gap – tunable from infrared to ultraviolet due to quantum confinement**

**Lowest Gaps vs. cluster size**



### Improvement in spectra with improved functionals

**Asymptotically correct form:  $V_s(r) \rightarrow 1/r$**   
(e.g., R. van Leeuwen and E. J. Baerends, Phys. Rev. A 49, 2421 (1994); M. E. Casida and D. R. Salahub, J. Chem. Phys. 113, 8918 (2000).)

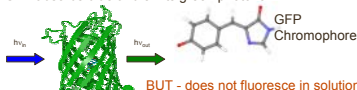


### Optical Response in Condensed Phases and Complex Environments - Nanoscale Optical Devices

**Example: Nanoscale wavelength conversion (GFP)**

Can we understand/design?

GFP absorbs blue and emits green photons.



**Dynamics is expensive** – Need new methods for excited states in condensed phases and large molecular assemblies – **MRSE** (Multireference reparameterized QM/MM semiempirical methods)

**MRSE** - More accurate than CASSCF for 1/10<sup>th</sup> the cost!

**Future work:** Haber et al. developed linear-scaling algorithms for wave propagation using discontinuous Galerkin finite elements in time and space.

- Convenient, parallel computation
- Adaptation of numerical mesh simultaneously in space and time.
- Collaboration under way to adapt the ideas to time-dependent quantum equations. (Haber, Johnson, Martin)



### Summary

We have identified fundamental failures of TDDFT – and steps toward better functionals for both ground and excited states. We are currently investigating multi-reference TDDFT analogs, current functionals, and the possibility of properly describing Berry's phase in a density functional. New approaches to time dependent calculations offer the possibility of important improvements in algorithms.

## Control of Charge and Spin in Quantum Electronic Devices

D. Das, J. N. Kim, J. P. Leburton, R. M. Martin and L. Zhang  
Departments of Electrical and Computer Engineering, Physics  
University of Illinois at Urbana-Champaign

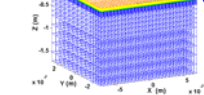
### Overview

- "Quantum Dots" are systems in which electrons are confined on nanoscale dimensions so that quantum effects are essential in actual devices
- Electron number, spin, and spatial extent can be controlled by applied voltages
- Can be used to control currents, e.g., single electron transistors
- Interactions between electrons lead to preferred spin states
- Spintronics -- Quantum Computers
- Challenges :
  - Create novel structures for control of charge/spin
  - Accurate theoretical treatment of strongly interacting electrons

### Simulation of a nanoscale quantum device

**Finite Element method for solution of coupled differential equations:**  
**Kohn-Sham equations for electrons**  
**Poisson equation for Coulomb Fields in Device**

**High resolution mesh:**  
5 x 10<sup>6</sup> mesh pts.  
(141x52x71)



-3D self-consistent **Kohn-Sham** equation within the effective mass approximation

- Exchange-Correlation included using the local spin density approximation **LSDA**

-3D **Poisson** equation w/classical (dopants) and quantum charges

-Device **boundary conditions** (Dirichlet&von-Neumann, no a-priori confining potential)

→ Eigen levels and Spin states – calculated as functions of gate voltages ( $V_g$ )

-**Slater rule** for electron charging:

- Total # of electrons=fct ( $V_g$ ),
- Total Spin = fct( $V_g$ )

### Quantum Monte Carlo simulations for electrons

**QMC** simulation – illustration of one step in the random walk of 3 electrons

### Comparison of methods:

#### Kohn-Sham density function equations

- Advantages:** fast, applicable to complex systems
- Disadvantages:** unknown accuracy, spin an symmetry may be qualitatively incorrect (Example at left: incorrect degeneracy in molecules)

#### Quantum Monte Carlo simulations

- Advantages:** most accurate method known for many interacting electrons, applicable to complex systems
- Disadvantages:** Depends upon the trial function – usually from DFT, previous work has relied upon model potentials or device potentials supplied by DFT calculations

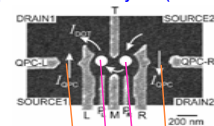
### References

Experiments by group of L. P. Kouwenhoven:  
J. M. Elzerman, et al., "Few-electron quantum dot circuit with integrated charge read out," Phys. Rev. B 67, 161308 (2003)  
Finite Element Method:  
P. Matagne and J.-P. Leburton, Phys. Rev. B 65, 235323 (2002).  
Previous collaborations comparing LDA/GMC:  
J. P. Leburton, S. Nagaraja , P. Matagne and R. M. Martin, Microelec J 34, 485-489 (2003)

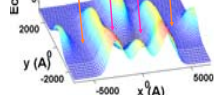
### Example of quantum device:

**Double dot – occupations controlled by gates – detected by currents  $I_{GPC}$  that sense the potentials due to electrons in the dots**

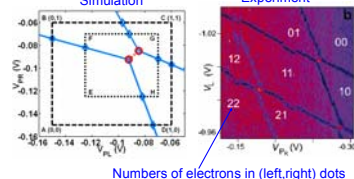
### Experimental circuit lay-out (Kouwenhoven)



**Potential profile in dot created in 2-DEG Simulation**



**Charge stability diagram – controlled by left and right "plunger gates"  $P_L$  and  $P_R$**



**Quantum Monte Carlo** simulation of electrons in the dot  
Most exact method known for many interacting particles

**New Approach: Classical Green Function Monte Carlo GFMC** simulation of Coulomb fields – exact simulation of interacting electrons in the real device with arbitrary metallic gates, dielectrics and boundary conditions

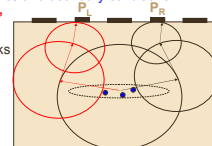
### "Walk on Spheres" – GFMC

Example of two walks that sense the gate voltages:

left ( $P_L$ )

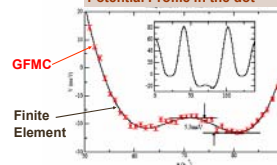
and

right ( $P_R$ )



### GFMC simulation of potential

**Potential Profile in the dot**



**Combined stochastic simulation in progress** – quantum electrons and the classical interactions and applied potentials within one algorithm

### Summary

We have demonstrated methods to solve the Kohn-Sham equations including all effects of the device structure. Now we are investigating the accuracy of the density functional approximations and developing methods to fully solve the interacting electron problem by Monte Carlo methods including the full device structure