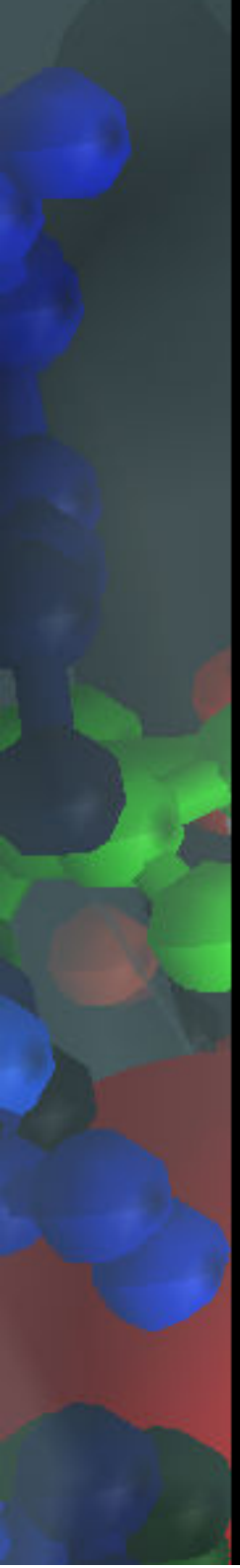

Quantum Monte Carlo study of photoprotection in photosynthesis

INCITE 1 Team

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The INCITE 1 Team

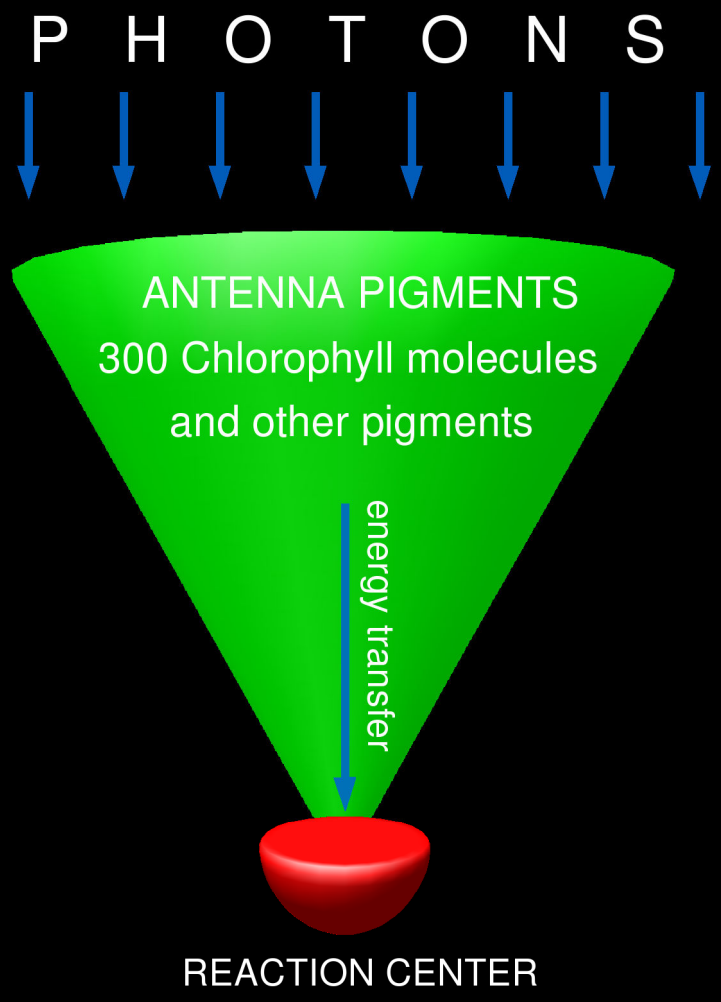
Alán Aspuru-Guzik, Graham Fleming, Brian Austin, William Lester, Romelia Salomón-Ferrer, Harsha Vaswani, Ricardo Oliva,

Not pictured: Dominik Domin, Michael Frenklach, David Skinner (NERSC) and the LBNL Visualization Group.

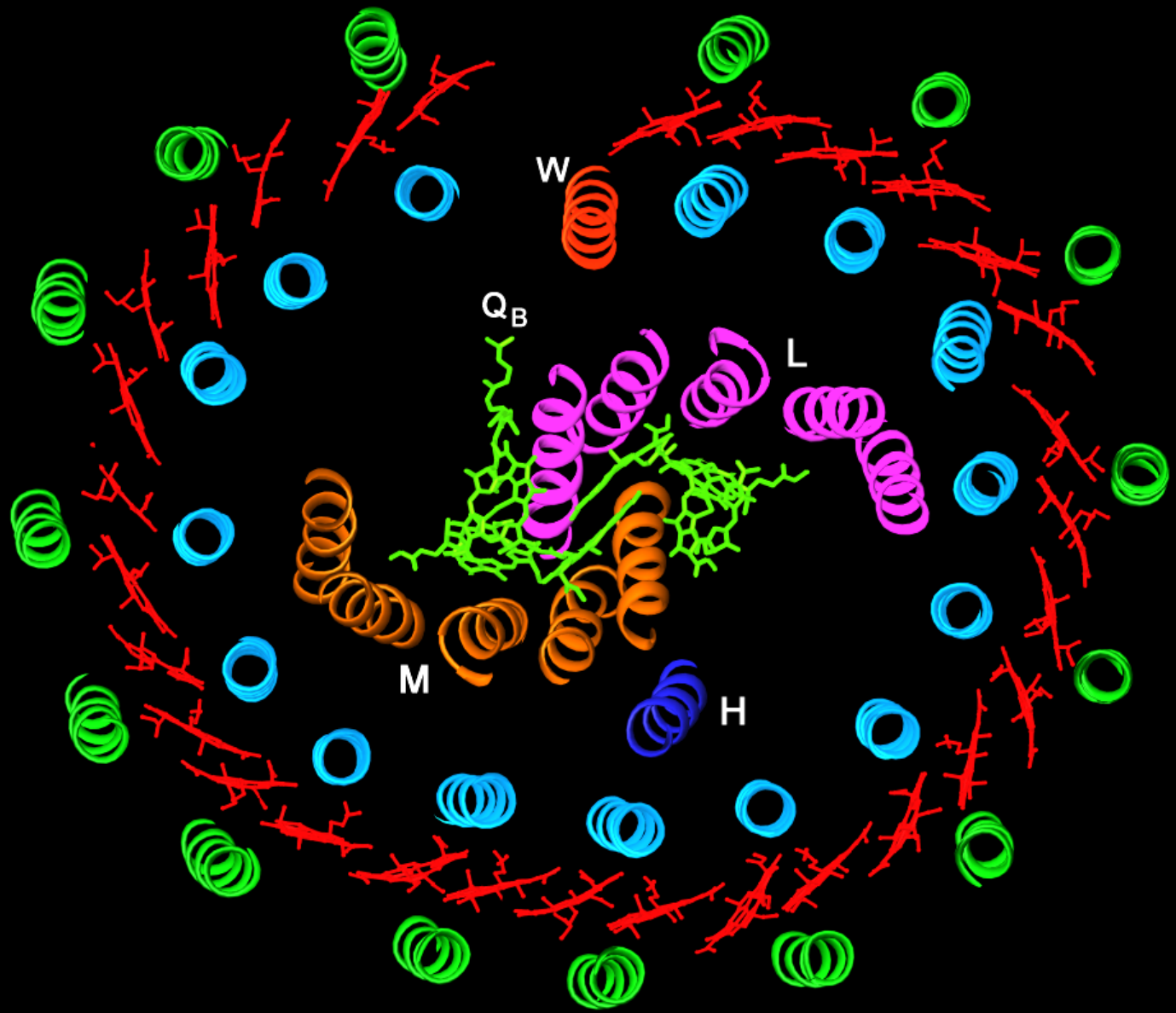
Photosynthesis 101

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

- Efficient:
  ~90% of energy absorbed is used to initiate photochemistry
- Fast:
  Turnover rate of photosynthesis
  ~ 100-300 /sec.
- Regulated:
  ~75% of absorbed energy can be dissipated with a 1 sec. response time



Reaction center of purple bacteria

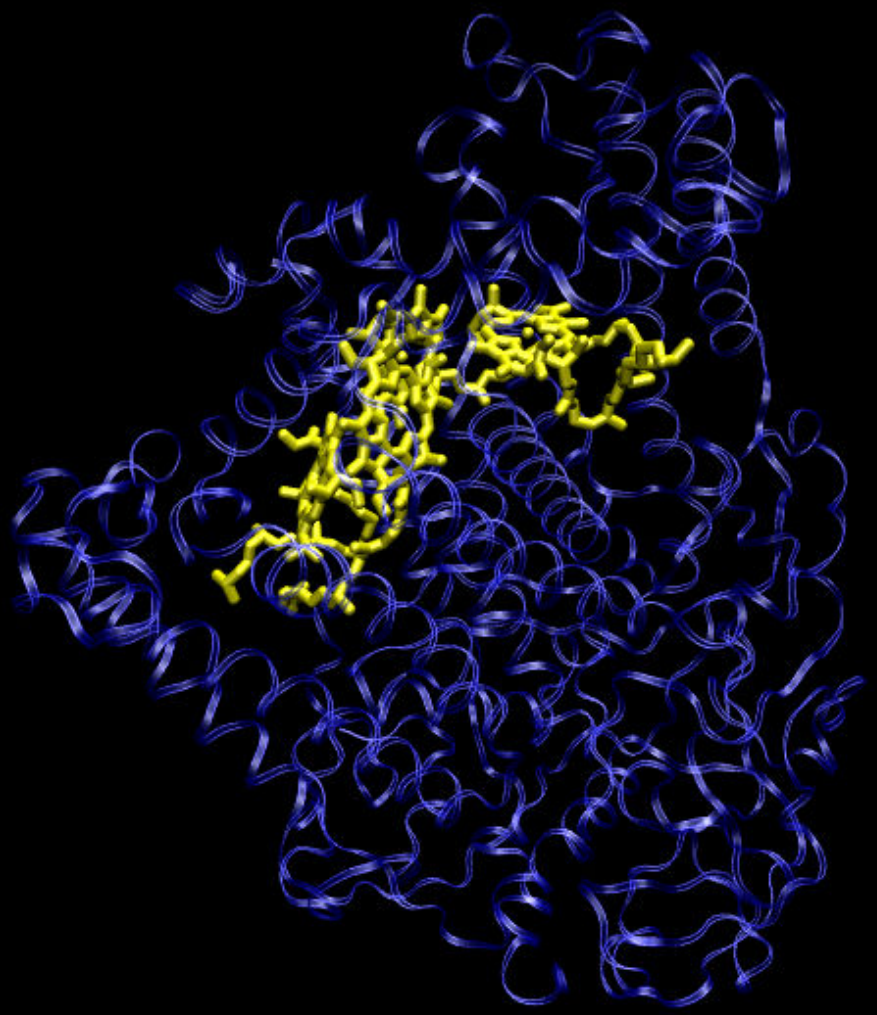


Roszak, *et al. Science*, 302, 1969 (2003)

Bacteriochlorophyll (BChl)

- Energy is transferred to the reaction center
- BChl molecules are excited into singlet excited states

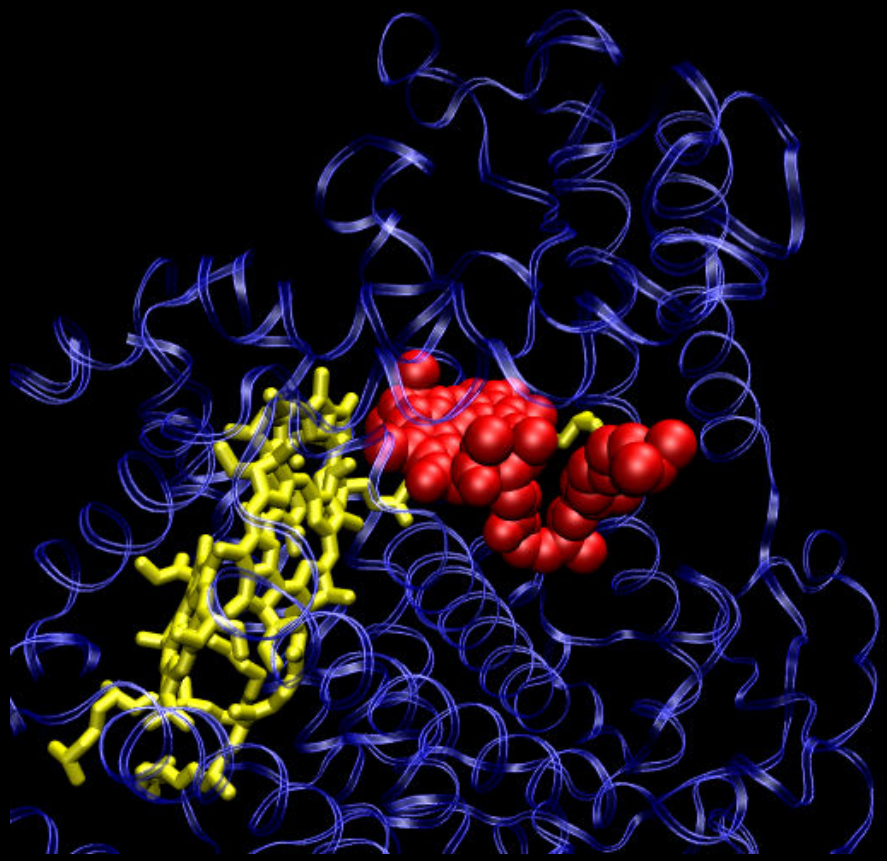
  $^1BChl + h\nu \rightarrow {}^1BChl^*$
- An electron is transferred from a pair of BChl to an electron acceptor molecule



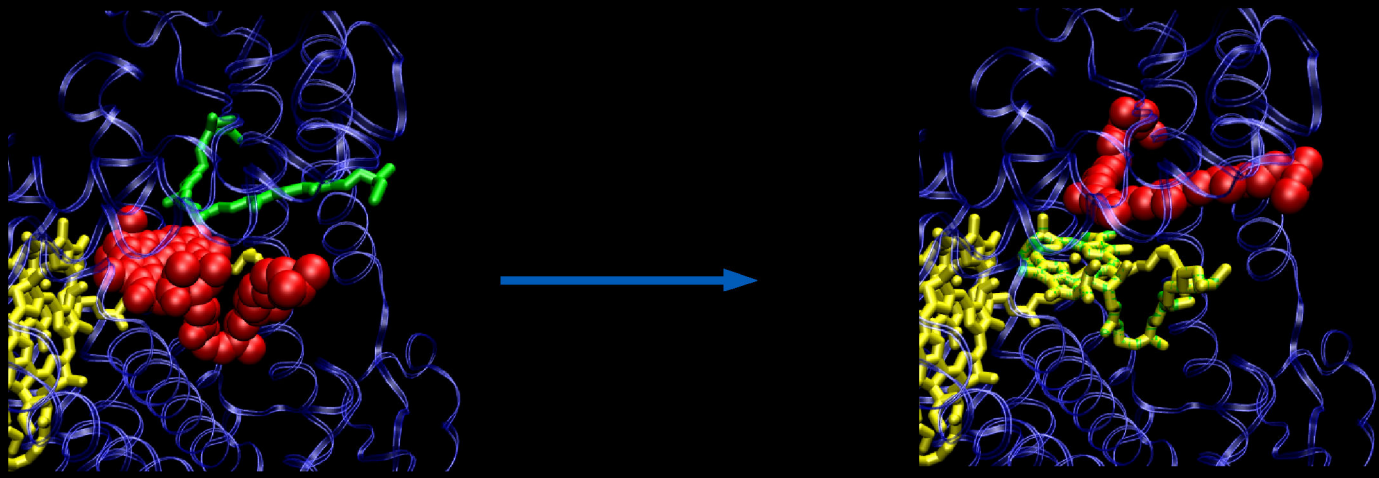
Excess light: Oxidative damage

- BChl can enter into a “forbidden” triplet state.
- In the triplet state, it can transfer energy to oxygen
- Singlet oxygen can damage the cell

$^{3}Chl^{*} + {}^{3}O_{2} \rightarrow {}^{1}Chl + {}^{1}O_{2}$



Photoprotection

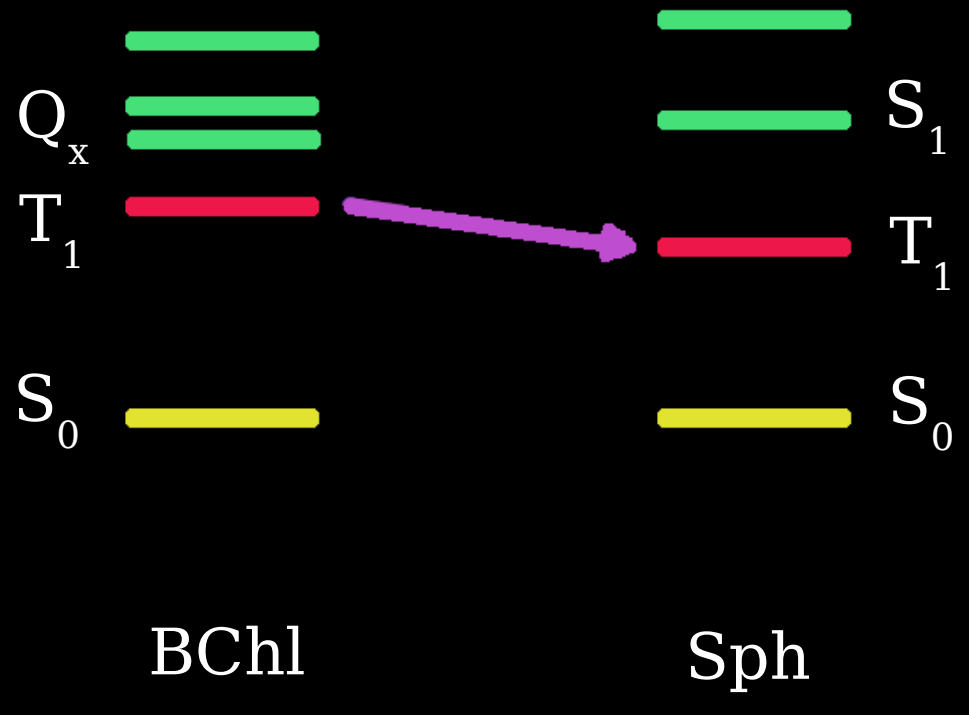


- Spheroidene (Spo) can quench the excitation of BChl
- The Spo excitation energy is dissipated safely as heat

$^{3}Chl^{*} + {}^{1}Car \rightarrow {}^{1}Chl + {}^{3}Car^{*}$

Scientific questions

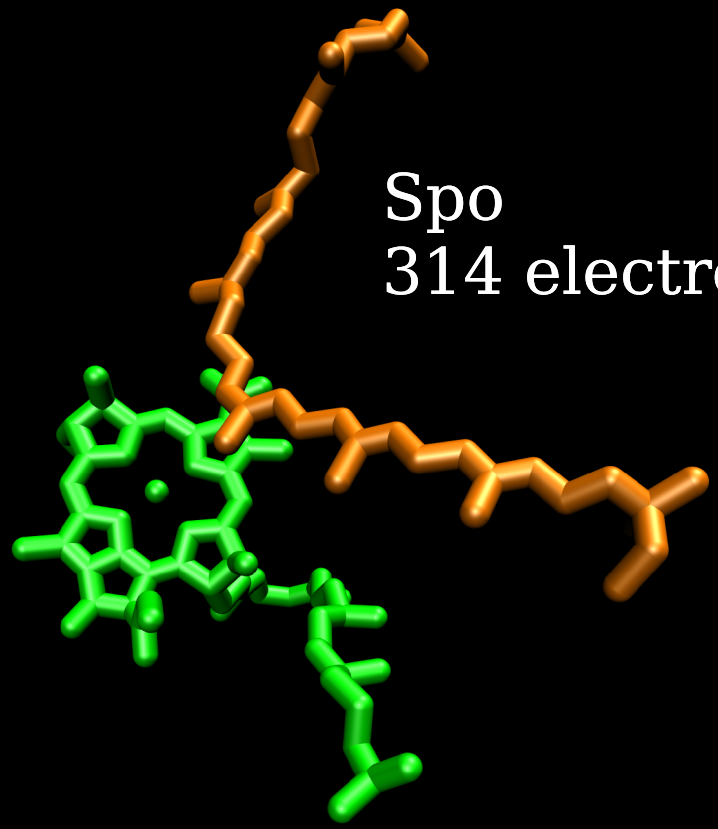
- What are the excitation energies involved?
- What is the rate of energy transfer?

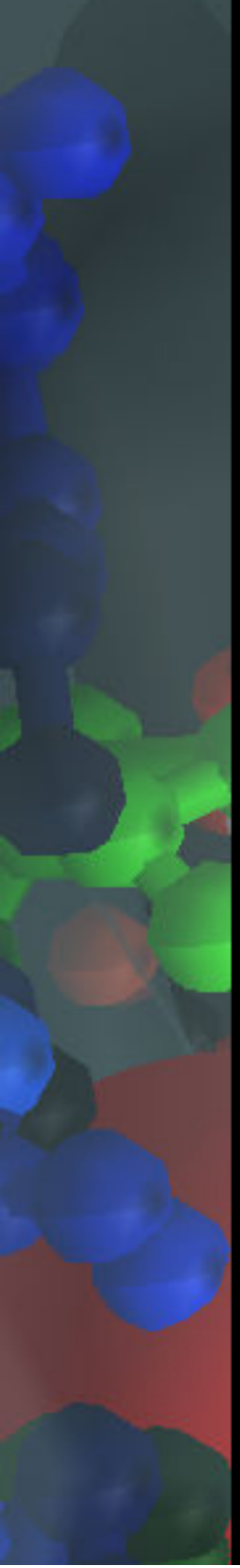


The plan

- Calculate BChl, Spo excitation energies separately
- Save wave functions for calculation of

  Bchl → Spo energy transfer rate
- 1,000,000 CPU hours at NERSC from DOE INCITE Award





Challenges

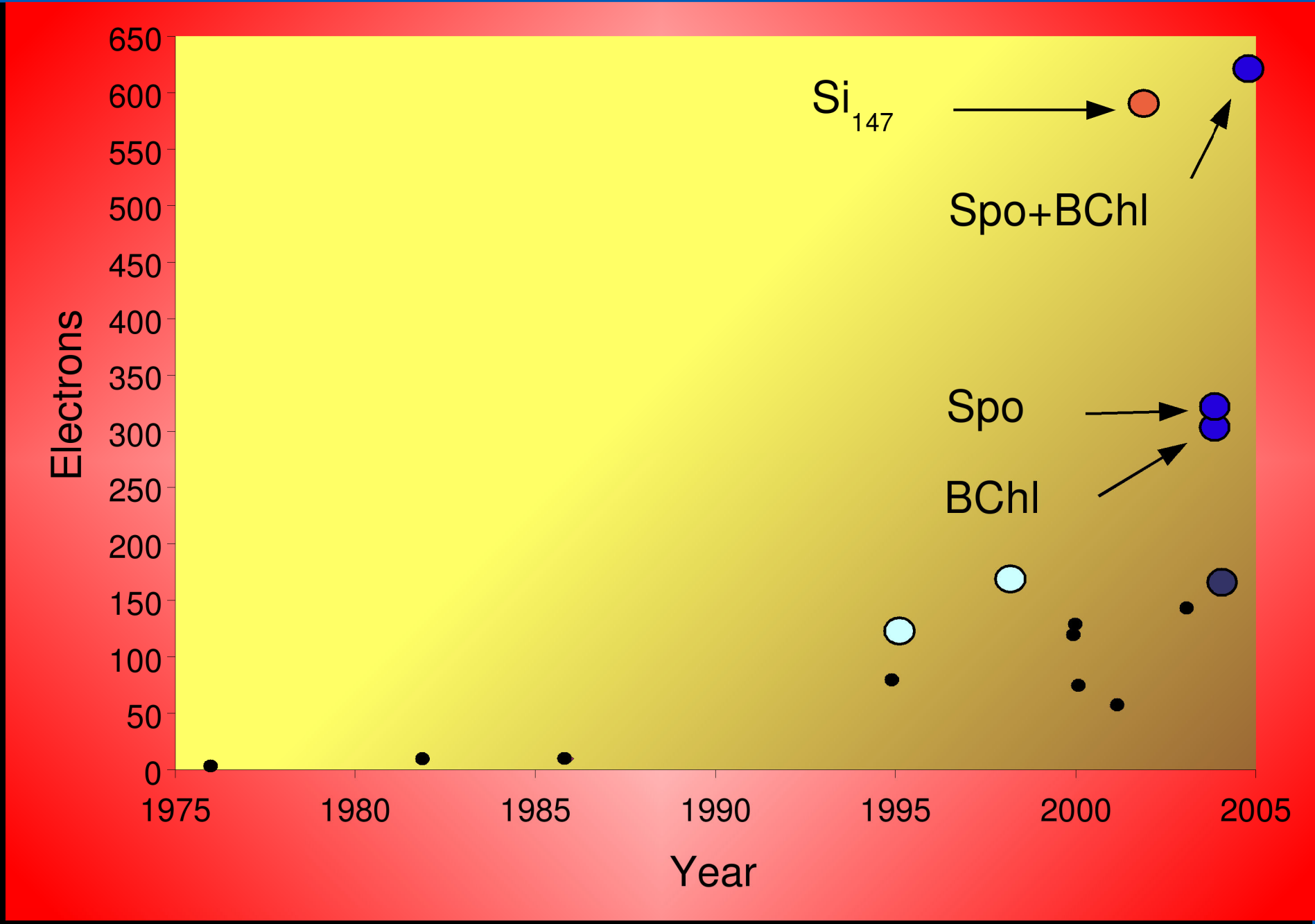
- Density Functional Theory is not accurate enough
- Rigorous correlated method is required
- Traditional correlated methods scale steeply with system size, e. g. CCSD(T) scales ~ N^7

* CCSD(T) has been described as the ”gold standard” of ab initio quantum chemistry – T. Dunning

Solutions

- Linear Diffusion Monte Carlo (LDMC) recovers 95-100% of the correlation energy
- Use of LDMC for excitation energies scales as ~ N^2
- Develop and use LDMC method for obtaining excitation energies and energy transfer rates.

QMC timeline



Coupled Cluster — Taylor et al. CPL 235, 558 (1995), Gwaltney et al. JCP 108, 6790 (1998)

Largest pseudopotential — Williamson et al. PRL 89, 196803 (2002)

Largest all-electron — Aspuru-Guzik et al. JCP 120, 3049 (2004)

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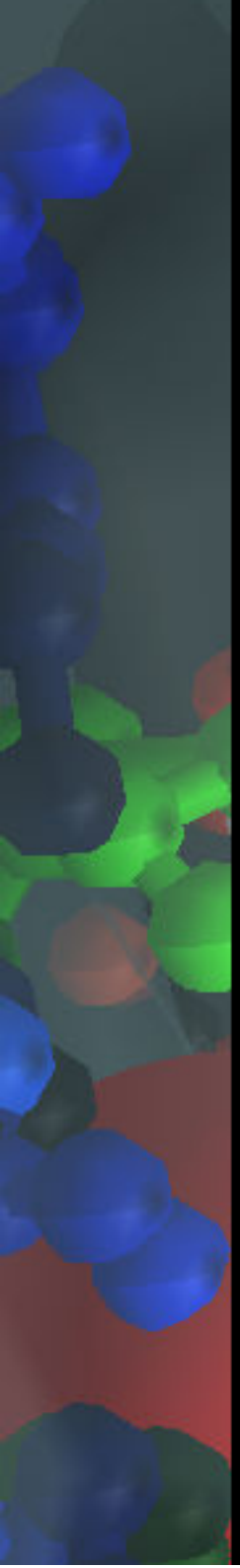
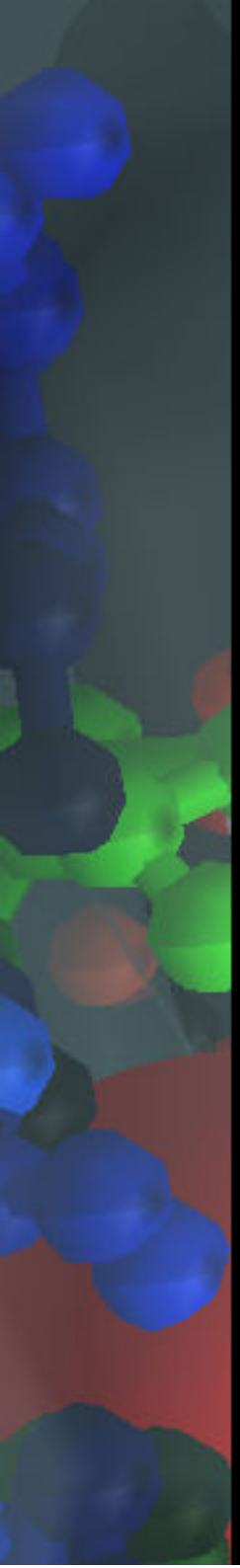


Numerical solution of the Schrödinger equation

- The method: Linear diffusion Monte Carlo.
- The Schrödinger equation is analogous to a diffusion equation in imaginary time.
- Solve the diffusion problem with sources and sinks using Monte Carlo sampling.



Diffusion Monte Carlo

The Schrödinger equation in imaginary time,

$$\frac{\partial \Psi(\mathbf{R},\tau)}{\partial \tau} = \frac{1}{2}\nabla^2 \Psi(\mathbf{R},\tau) - V(\mathbf{R})\Psi(\mathbf{R},\tau)$$

is realized stochastically as

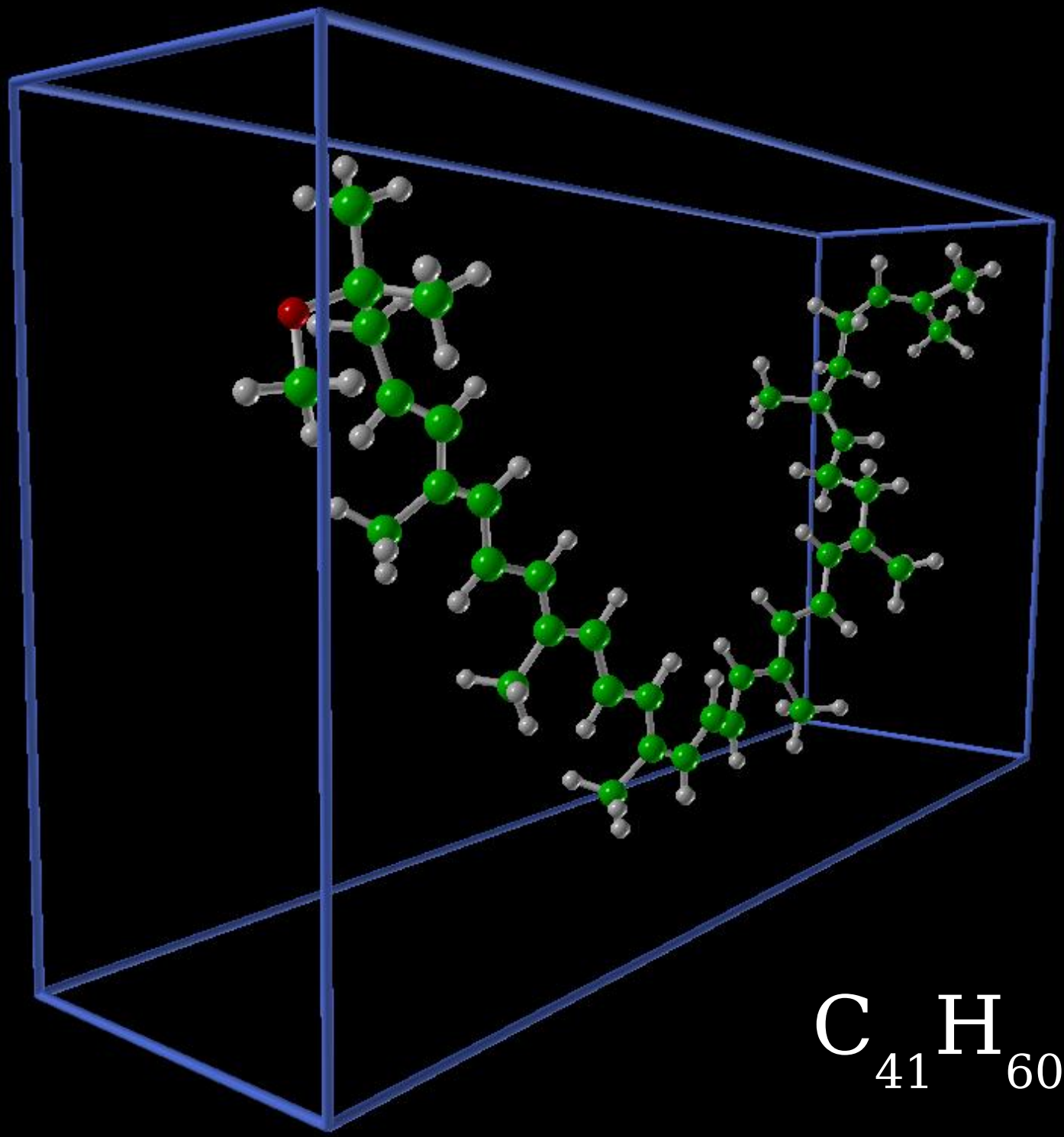
$$\frac{\partial \Psi(\mathbf{R},\tau)}{\partial \tau} = \frac{1}{2}\nabla^2 \Psi(\mathbf{R},\tau)$$

diffusion (random walk)

$$\frac{\partial \Psi(\mathbf{R},\tau)}{\partial \tau} = -V(\mathbf{R})\Psi(\mathbf{R},\tau)$$

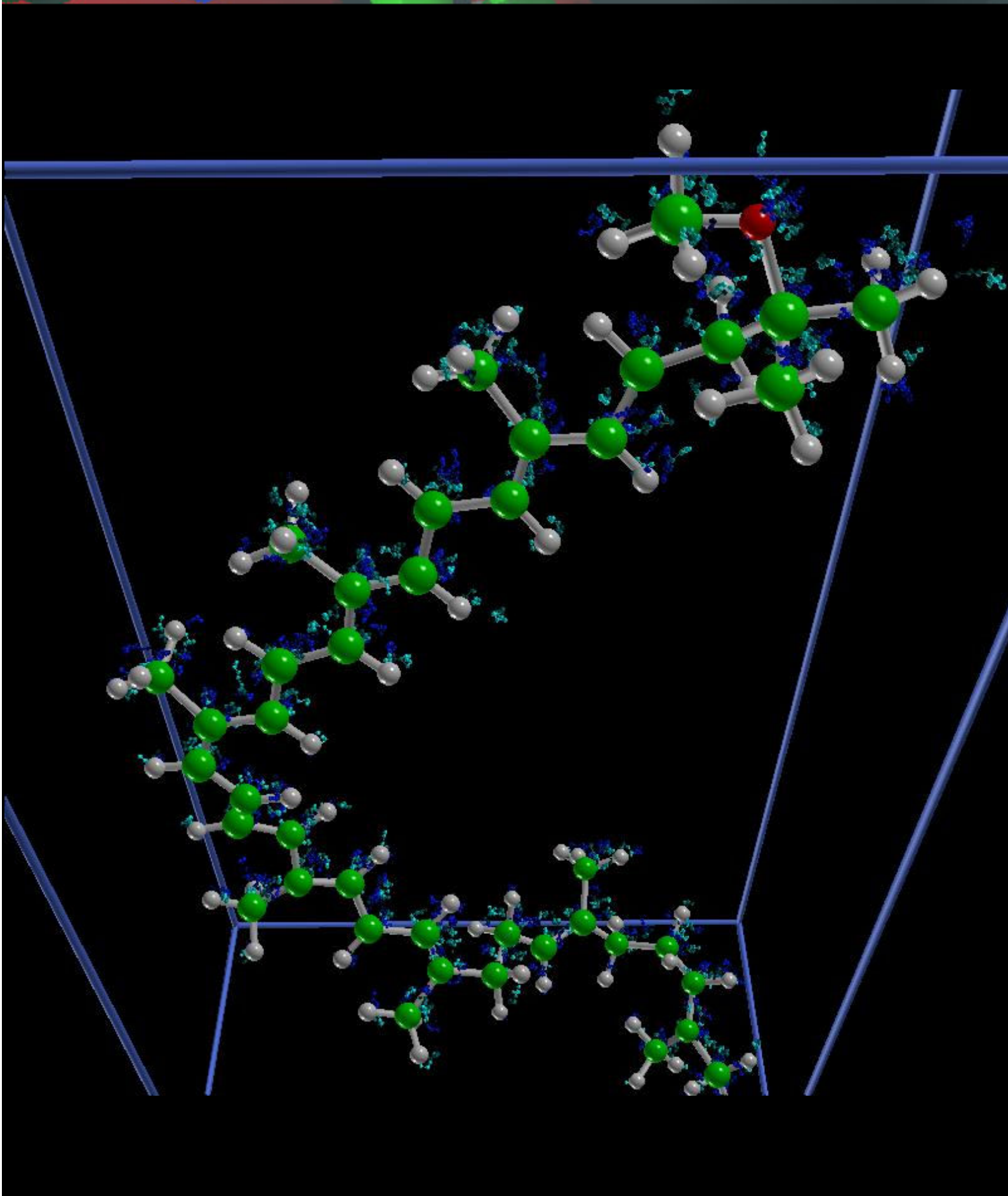
birth and death (first order kinetic process)

The nuclei

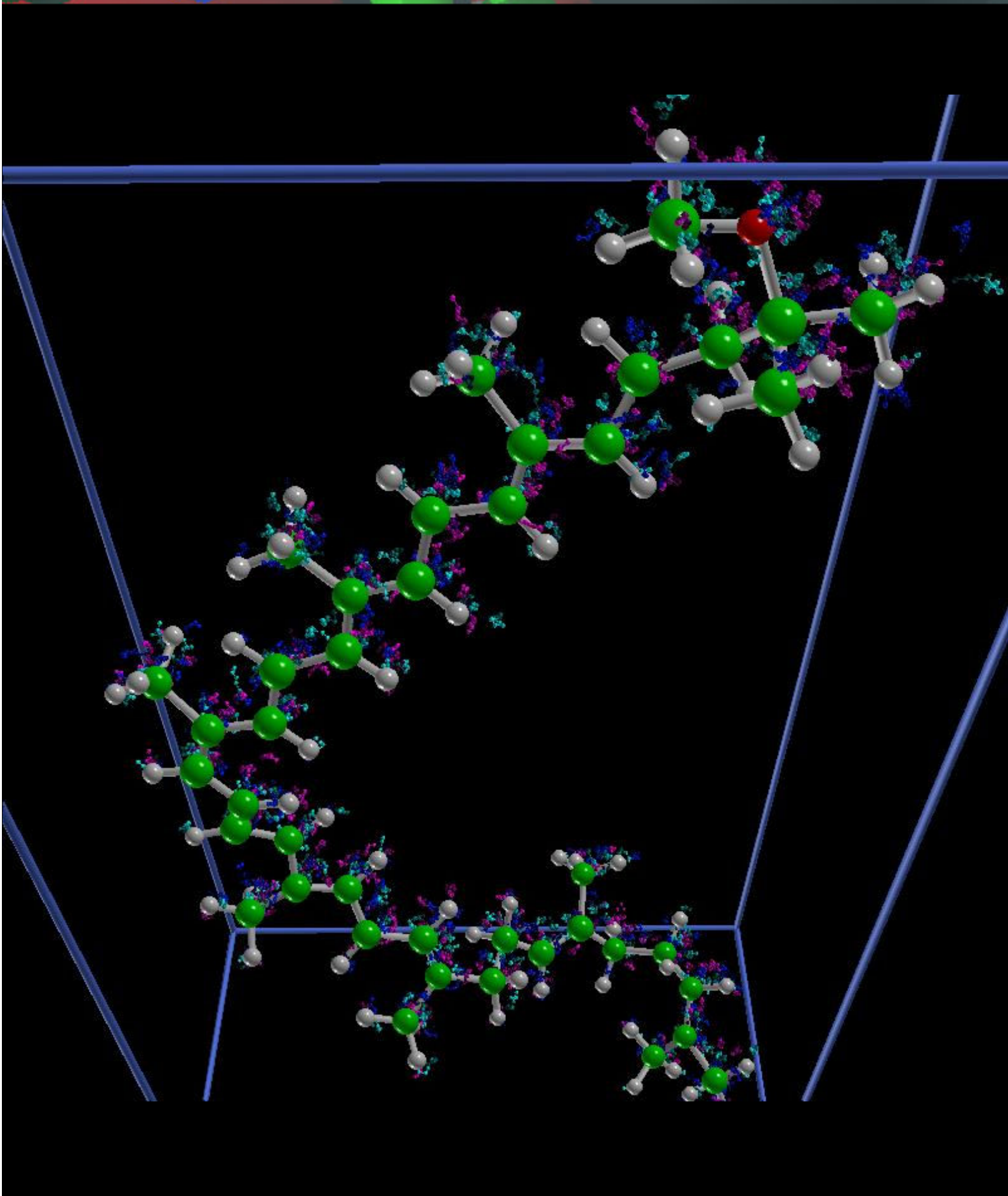


$C_{41}H_{60}O$

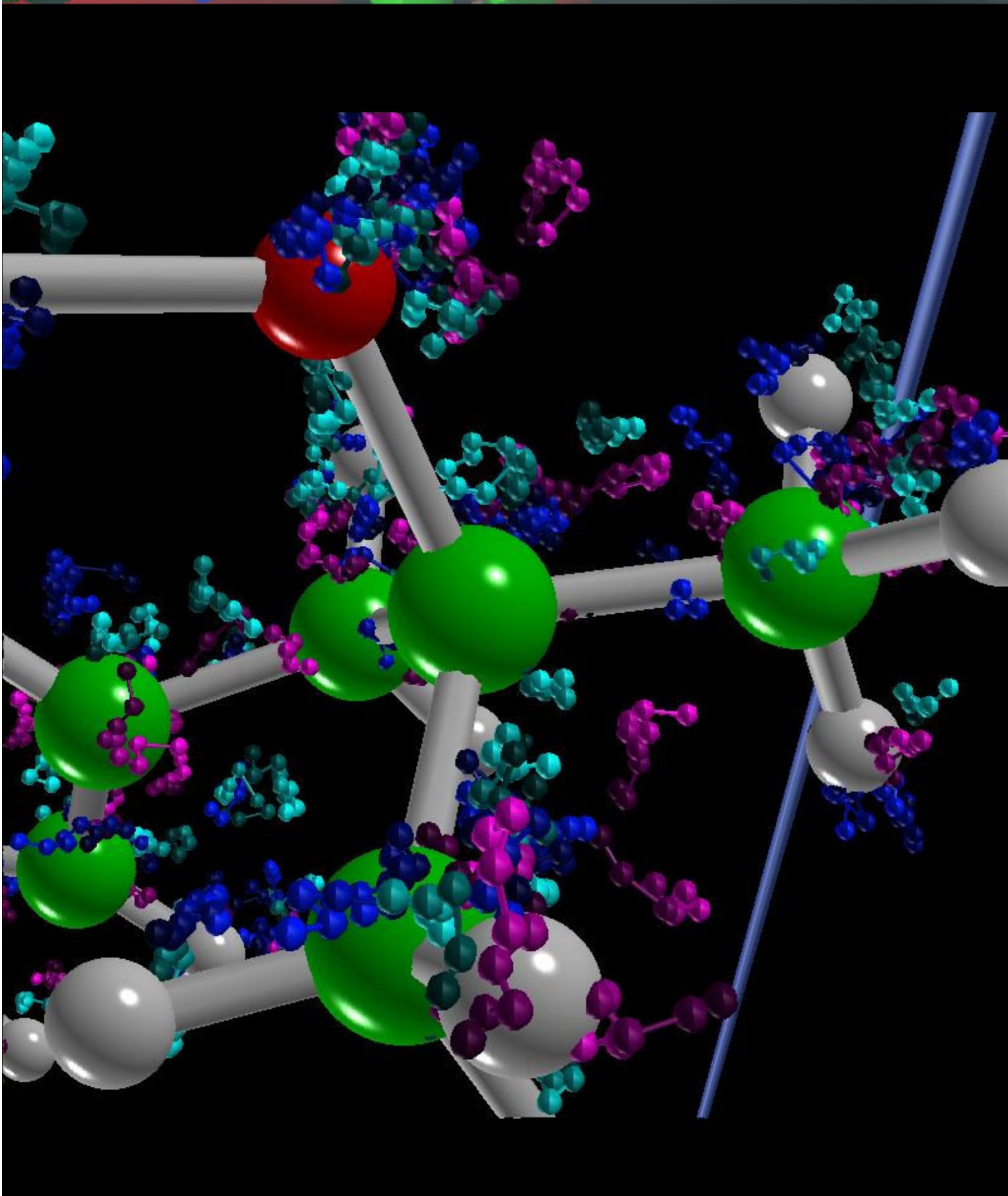
The electrons and nuclei



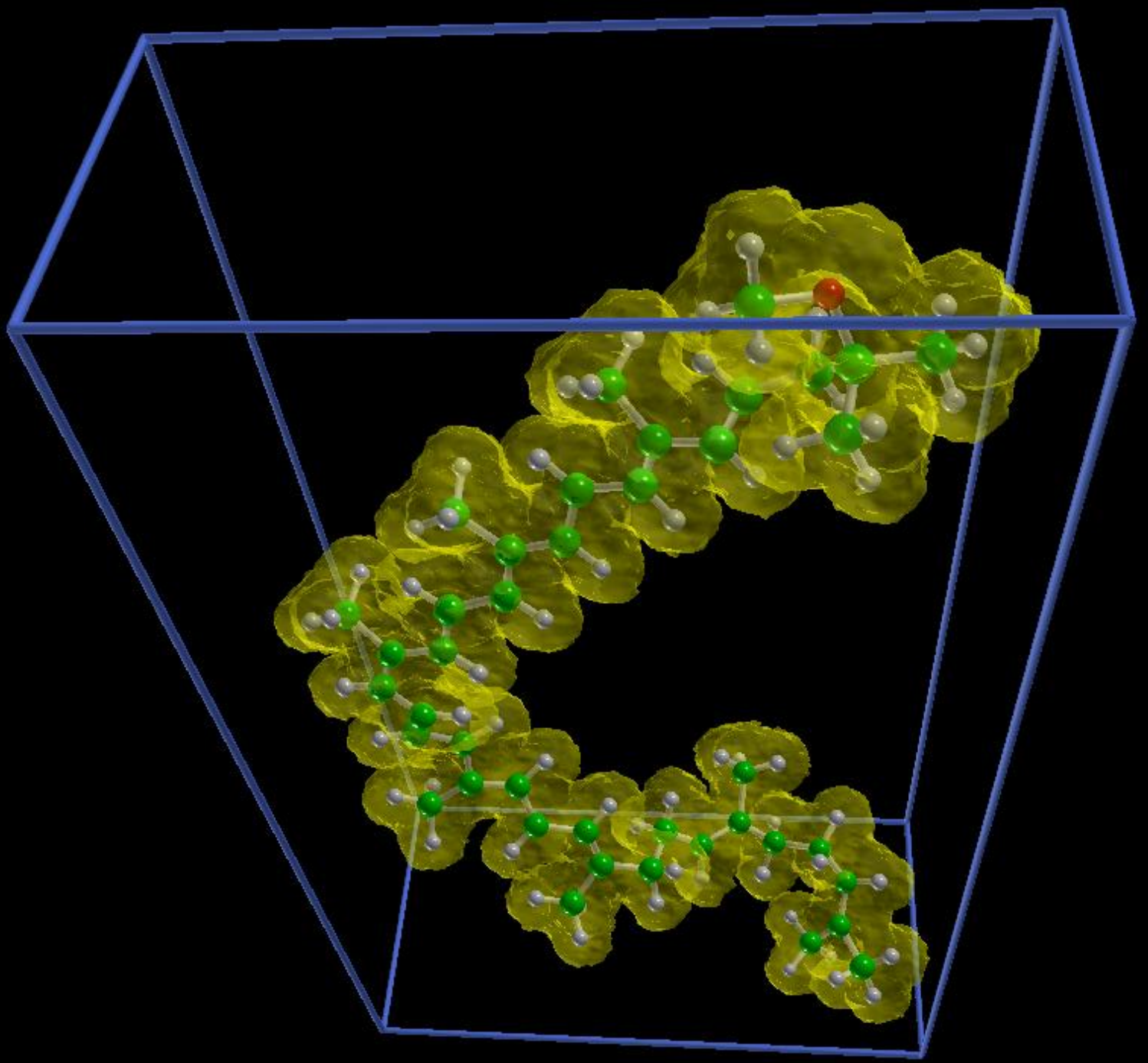
Additional random walker



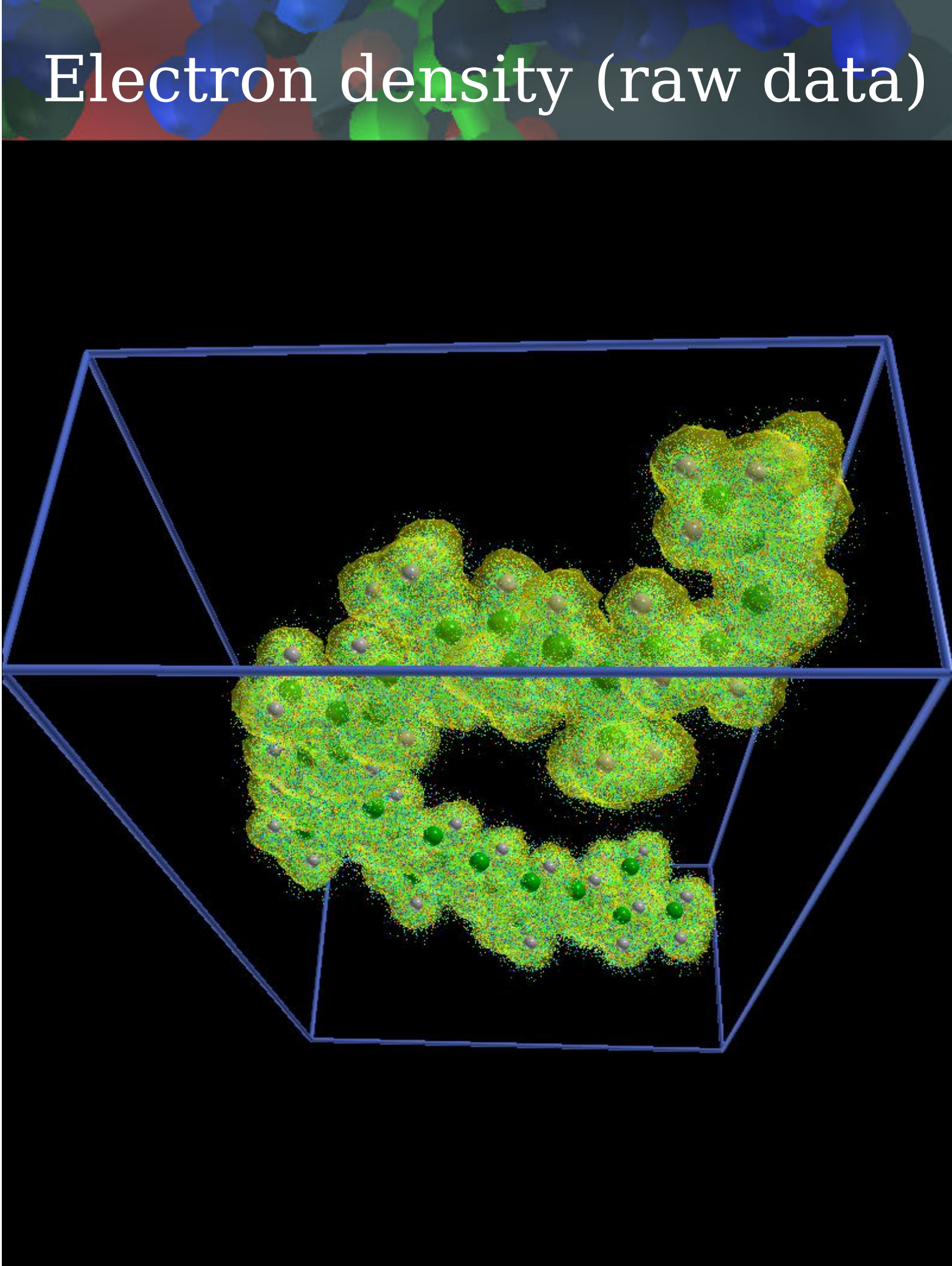
Close up view



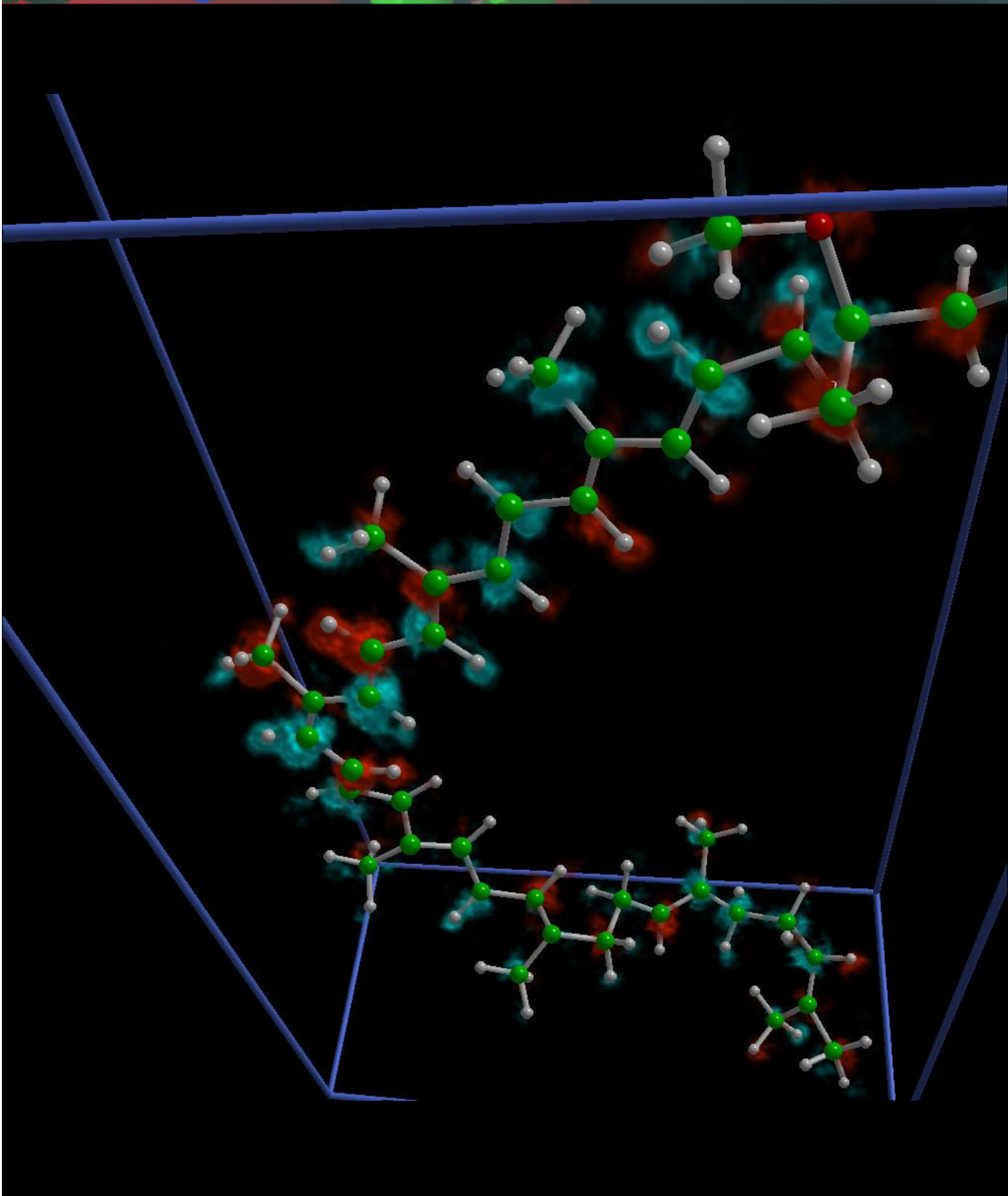
The electron density

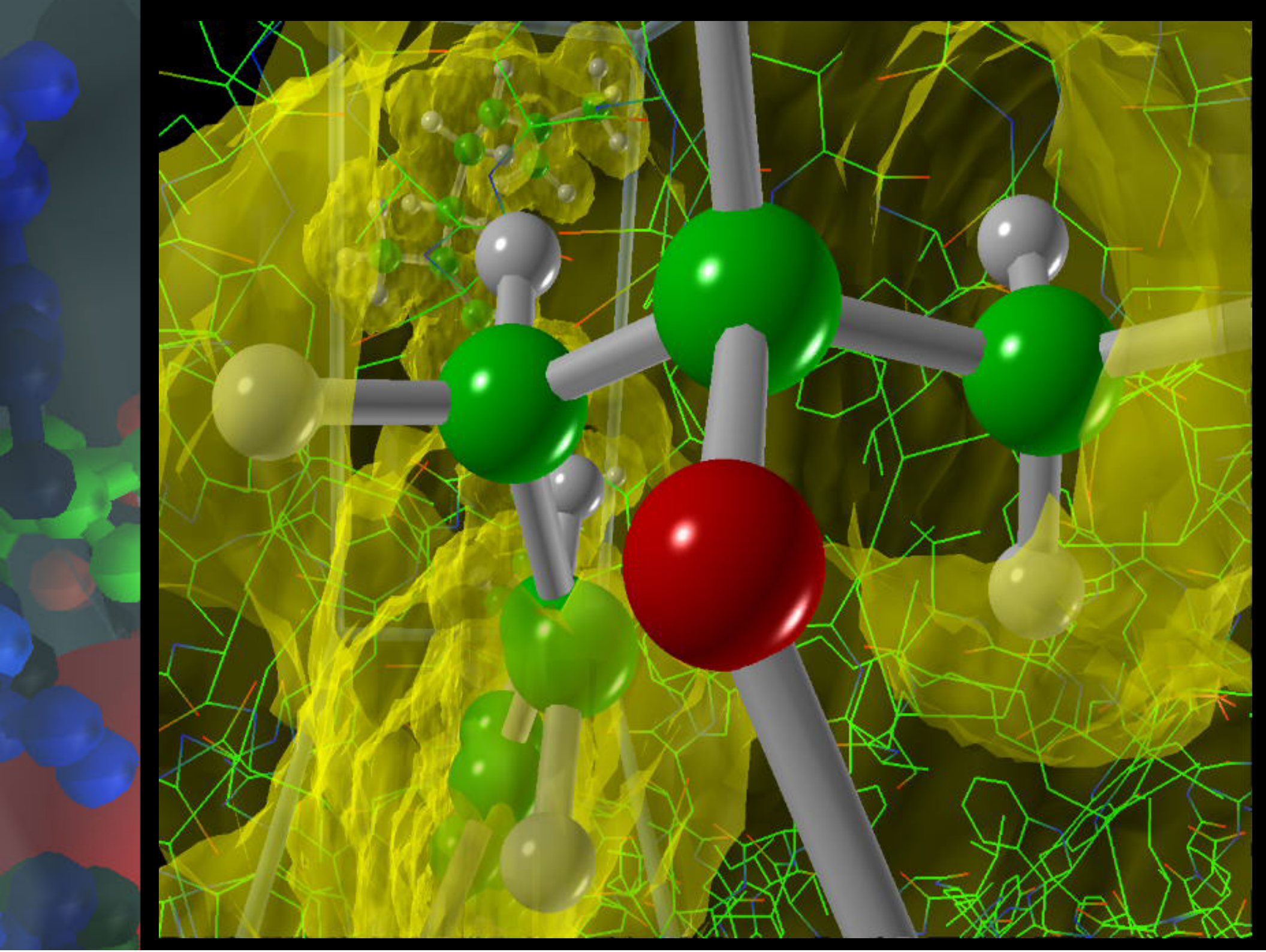


Electron density (raw data)



The spin density



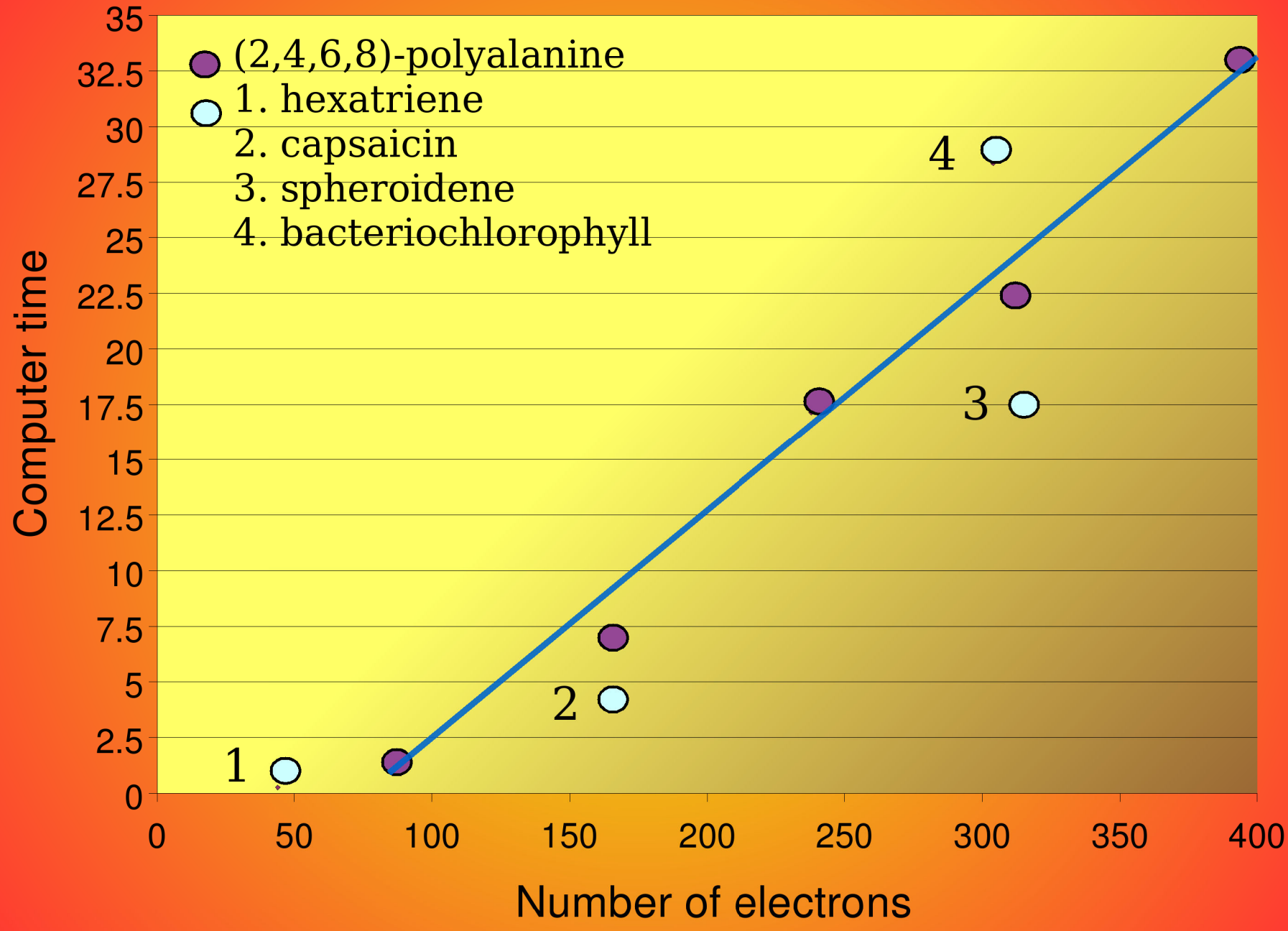


Code development under INCITE

- Linear-scaling QMC
- Improved random walk algorithms
- Improved correlation functions
- Improved I/O performance

Zori v 0.92
“lucky bird”
http://zori.aspuru.com

Linear Diffusion Monte Carlo



- Sparse matrix-based evaluation of the wave function
- 10x speedup over original algorithm

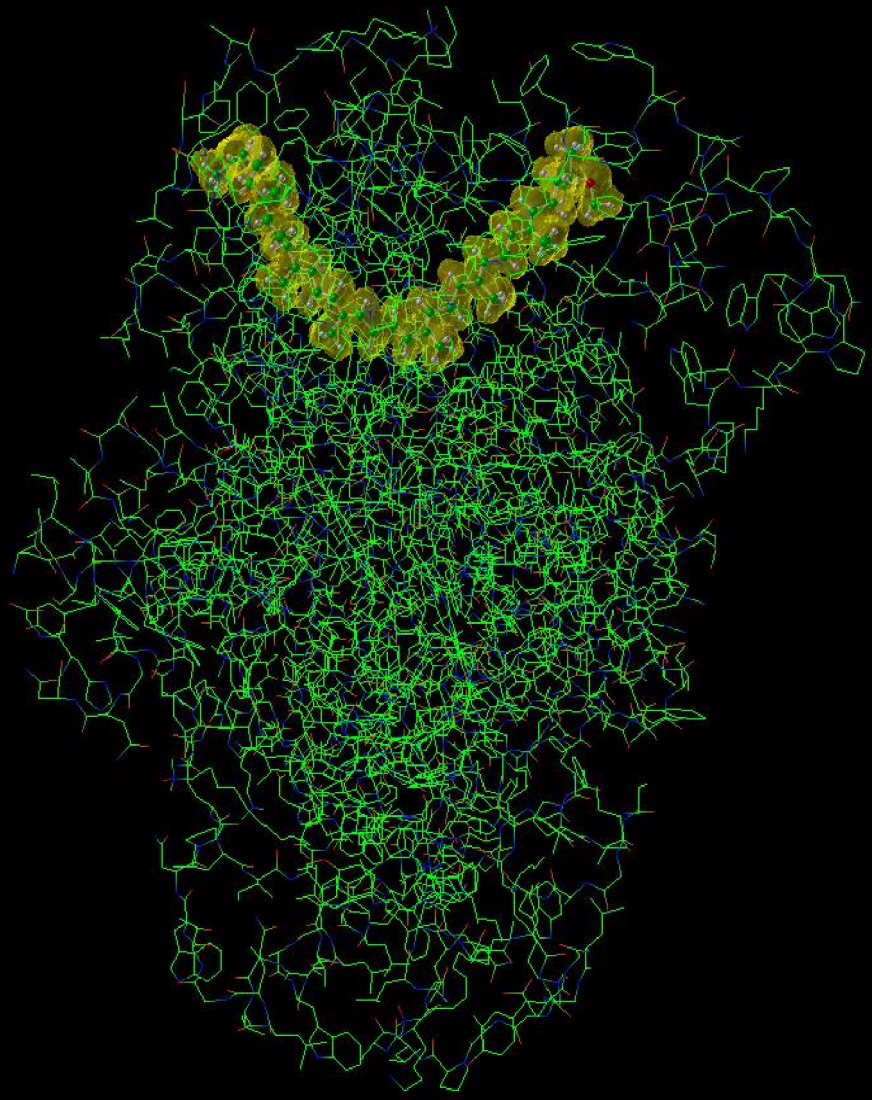
What's next?

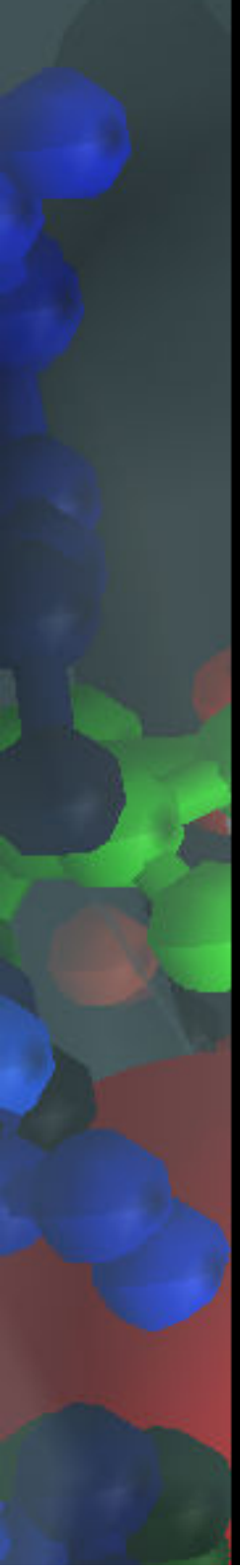
- Study systems of thousands of electrons (harness the power of architectures such as Blue Gene)

- Develop optimal QMC methods for excited states of large molecules

- Embedding

- Solvent effects





Conclusions

- We are studying systems 4 times larger than in 2003
- Next, focus on calculation of energy transfer rate and computation of singlet excited states
- New pedagogical tools were developed! Now one can study electron correlation visually and gain new insights

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