

# *Perspectives on computational quantum chemistry*

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## *Chemistry and mathematics*

“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible— it would occasion a rapid and widespread degeneration of that science.”

Auguste Comte, 1830.

## *Quantum mechanics and chemistry*

“...in the Schrodinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure”

but...

“... the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique.”

G. N. Lewis, J. Chem. Phys. 1, 17 (1933).

## *Computing and chemistry*

"In conclusion, I would like to emphasize my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory, for increasingly many facets of chemical information, is already at hand. There is only one obstacle, namely, that someone must pay for the computing time."

Robert Mulliken. Nobel Prize address, 1966.

# *Dreams: perfect chemistry from first principles*

- Many-body Schrödinger equation is a partial differential equation in  $3n$  unknowns—the positions of the electrons.
  - Exact (brute force) solution is exponentially difficult.

- Full configuration interaction (FCI).

- Exact solution in a finite basis of  $N$  1-electron functions

$$\hat{H}\Psi = E\Psi \rightarrow \mathbf{H}\mathbf{c} = E\mathbf{c} \quad \frac{N!}{n!(N-n)!} \text{ terms}$$

- $\mathbf{c}$  contains coefficients of every possible configuration
  - billions of terms, for 2 or 3 atom molecules (!!)
- Approximations are essential\*. Accuracy vs feasibility.

## *Aside\*: quantum computers and quantum chemistry*

- FCI requires polynomial effort on a quantum computer!
  - Number of **qubits** scales linearly with problem size
  - Number of **gates** scales polynomially
- Algorithm:
  - **Prepare** a wavefunction (e.g. mean-field)
  - **Propagate** the wavefunction
  - Sample the phase of the wavefunction to **read out** energy
- Proof of concept:
  - Water in minimum basis to 1 microHartree (12 qubits)
  - LiH in double zeta basis to 1 microHartree (15 qubits)

# *Reality: well-defined theoretical models*

- Wavefunction-based electronic structure theory:

- Minimize the energy by varying the wavefunction
- Tremendously complicated unknown function:

$$\Psi = \Psi(r_{\sigma_1}, r_{\sigma_2}, \dots, r_{\sigma_n})$$

- Modeling the wavefunction yields “model chemistries”

- Density functional theory

- The unknown is very simple:  $\rho = \rho(r_{\sigma})$
- Hohenberg-Kohn theorem guarantees that:  $E = E\{\rho(r_{\sigma})\}$
- True functional is unknown and probably unknowable
- Modeling the functional gives DFT model chemistries.

# *Density functional theory*

- Absolutely predominant in condensed matter physics
- Merely predominant for molecules, surfaces, and nanomaterials
- Strengths of present-day DFT:
  - It is the sweet spot between accuracy and feasibility
  - “Includes electron correlation at mean-field cost”
- Weaknesses of present-day DFT:
  - Not systematically improvable
  - Self-interaction errors (exchange functional)
  - Inadequate to treat strong and/or non-local correlations



# *Wave function approaches to electronic structure*

- Hartree-Fock (MO) theory (mean field):  $A^3$ - $A^4$  cost.
  - HF: 99%! “Correlation energy” is roughly 1 eV per pair.
- Perturbative treatment of the electron correlations:  $A^5$ 
  - MP2: 80% of the last 1%. “Pair correlations” (doubles).
- Treat single & double substitutions self-consistently:  $A^6$ 
  - CCSD: 95% of the last 1%.
- Correct for the triple substitutions perturbatively:  $A^7$ 
  - CCSD(T): > 99% of the last 1%. Chemical accuracy.
- Systematically improvable -- at a computational cost!

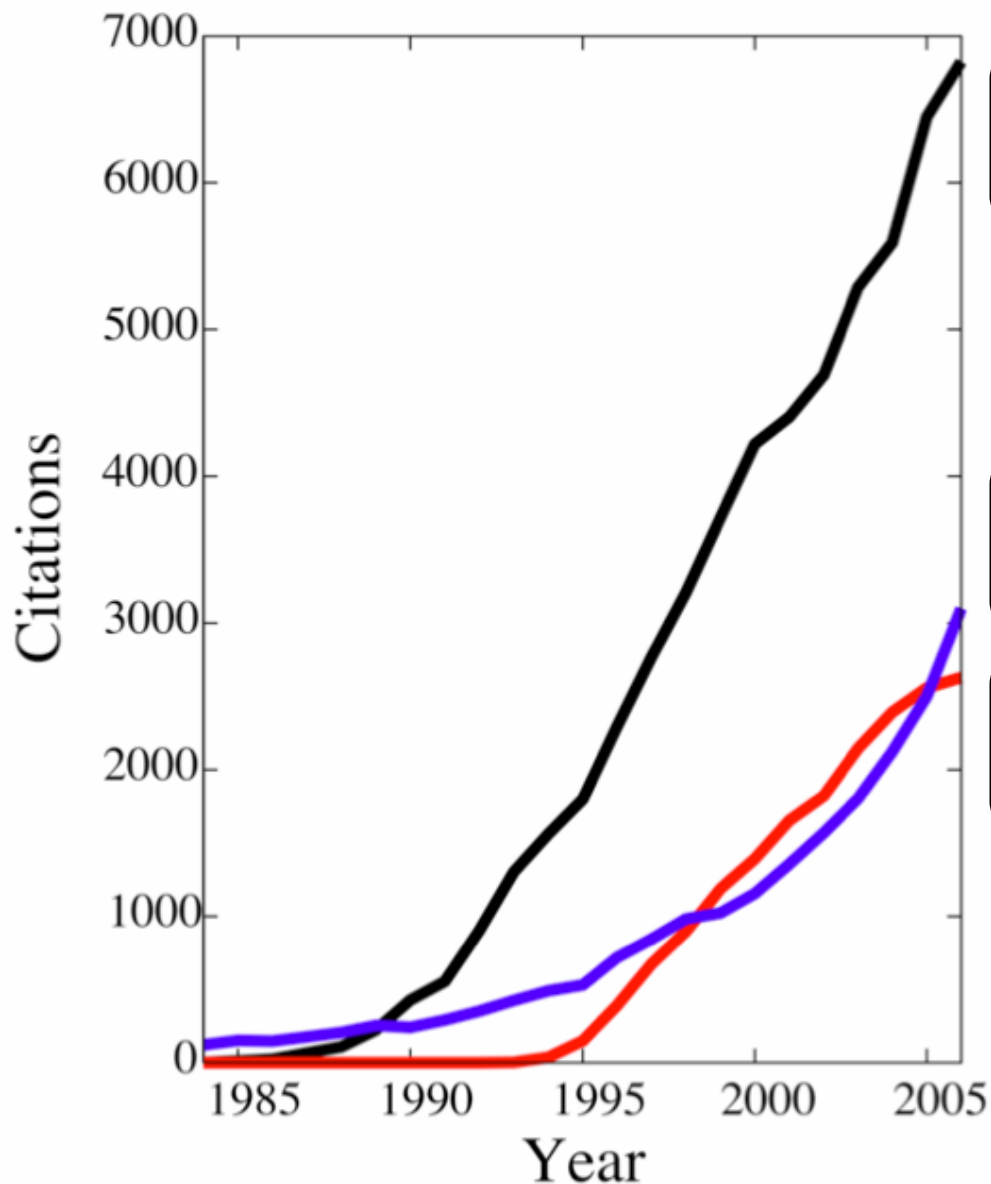
# *Software platform: Q-Chem 3.0*

“Advances in methods and algorithms in a modern quantum chemistry program package”

Y. Shao, L. Fusti Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr, R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer III, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon

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# *Quantum chemistry calculations are ubiquitous*

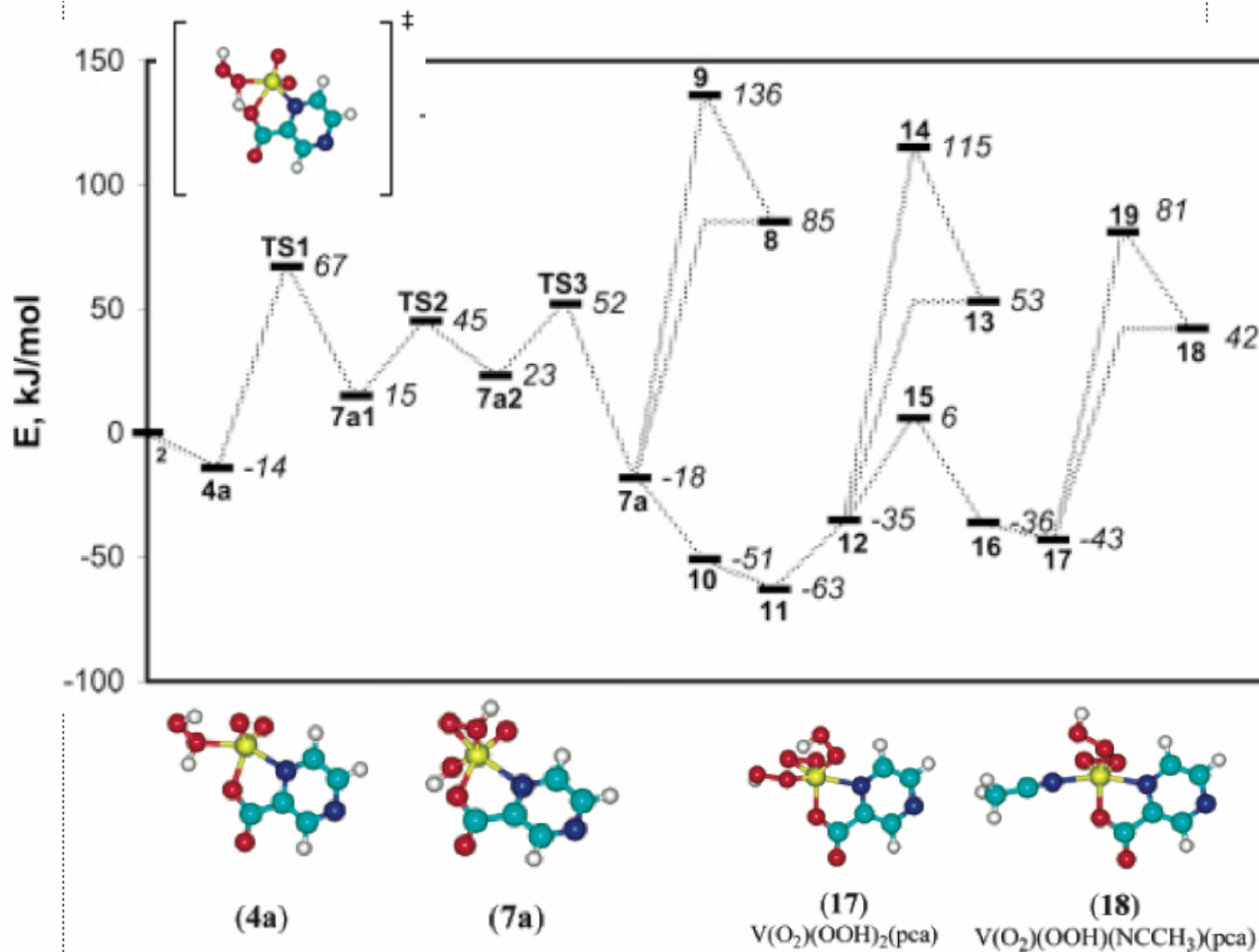


Program  
citations

GGA  
Citations (DFT)

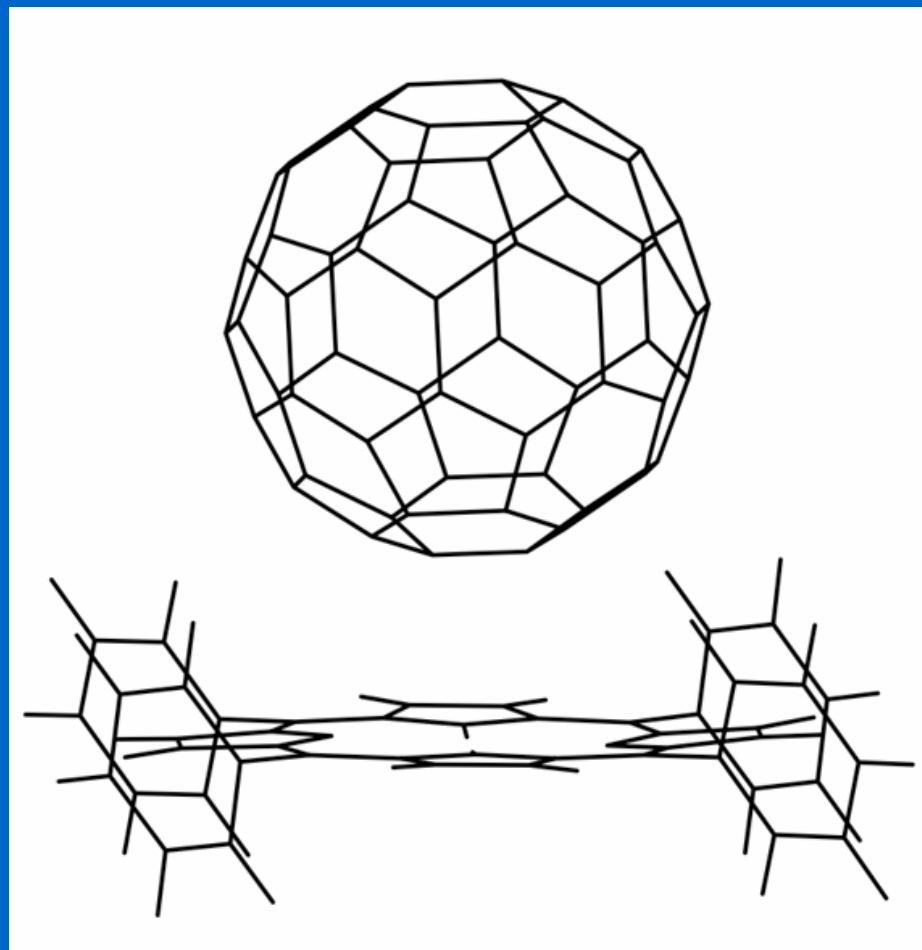
Hybrid GGA  
Citations (DFT)

# DFT usage example: homogeneous catalysis



# *Wavefunction theory approaches large systems*

- Example: fullerene-porphyrin binding energy
- Basis sets:
  - cc-pVDZ, cc-pVTZ
  - counterpoise correction
  - 3520 basis functions**
- SOS-MP2: binding is  
-31.5 kcal/mol



## *Lessons in mass usage*

- Vast majority of users are not expert.
  - No undergraduate training in computational chemistry
  - Situation is slowly changing -- for the next generation...
- A crisis of competence?
- No evidence of it so far.
  - Aided by simplicity of “theoretical model chemistries”
    - Atoms, electrons, basis set & correlation model
  - And by intrinsically skeptical experimental users.

## *Future methods development*

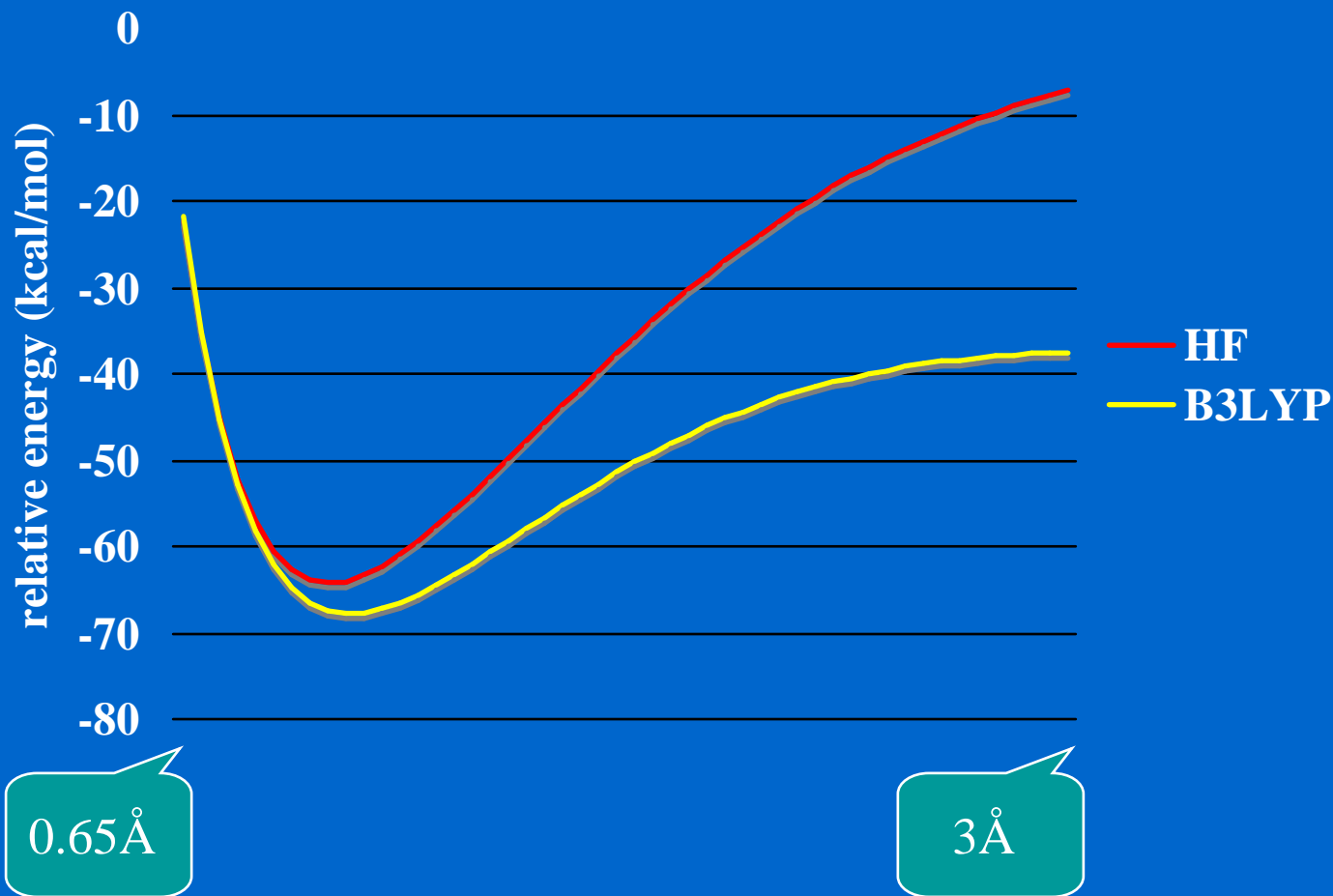
- Quantum chemistry is mature enough to support tens of programs and tens of thousands of users.
- Where are the frontiers in the methods? Have we reached a level of maturity similar to x-ray crystallography, NMR, and mass spectrometry?
- Maturity is deceptive -- our users are smart enough to (usually) avoid the serious current limitations of current methods. And even our algorithms are in a state of flux.

# *Challenges for density functional theory*

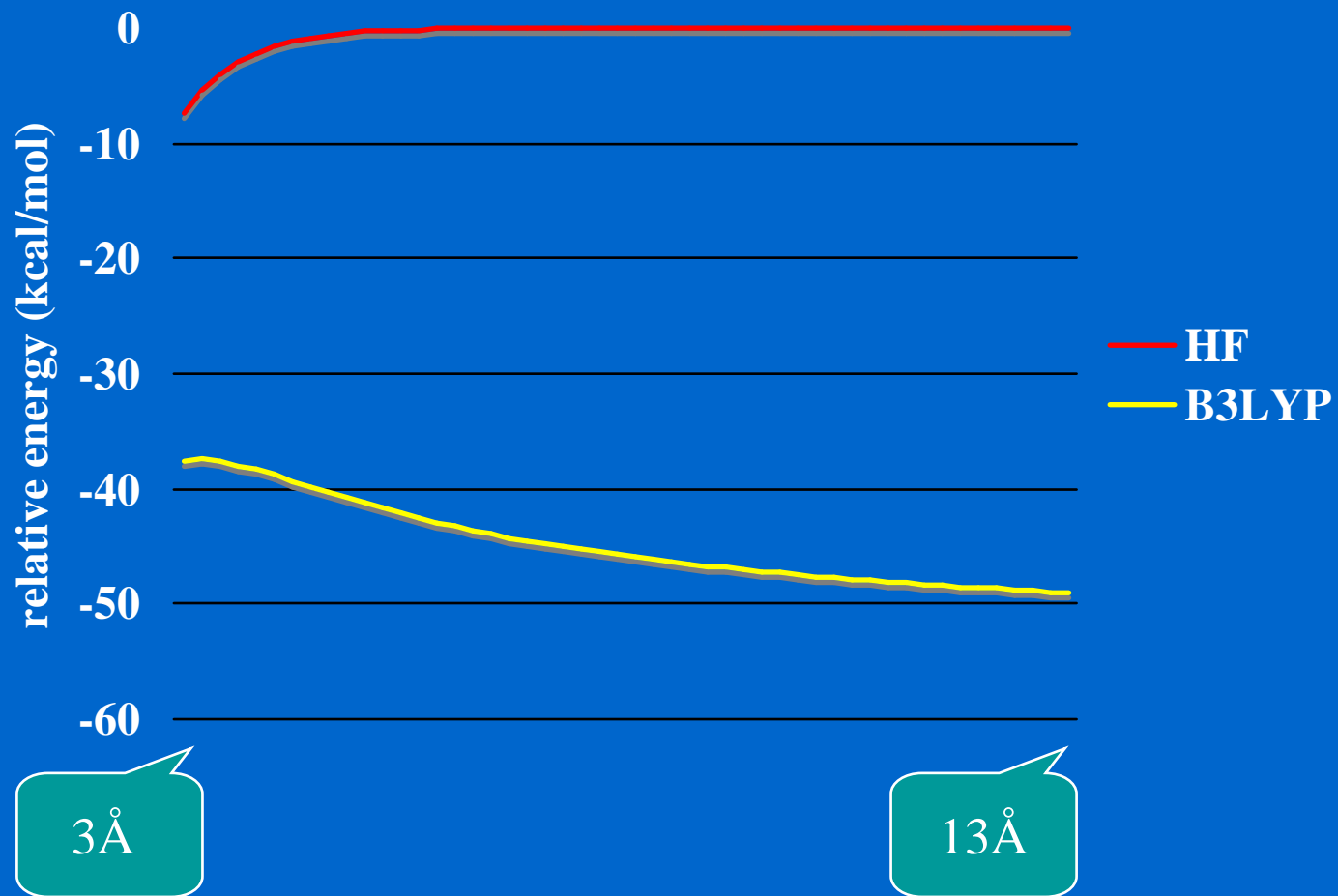
- Lack of systematic improvability confronts...
  - (1) Limitations of the exchange functional
    - Self-interaction
  - (2) Limitations of the correlation functional
    - London forces
    - Strongly correlated systems
- “Fast” algorithms -- changing (almost) everything
  - From cubic scaling to linear (with high precision!)



# *B3LYP dissociation of $H_2^+$ (0.65Å to 3Å)*



# *B3LYP dissociation of $H_2^+$ (3Å to 13Å)*

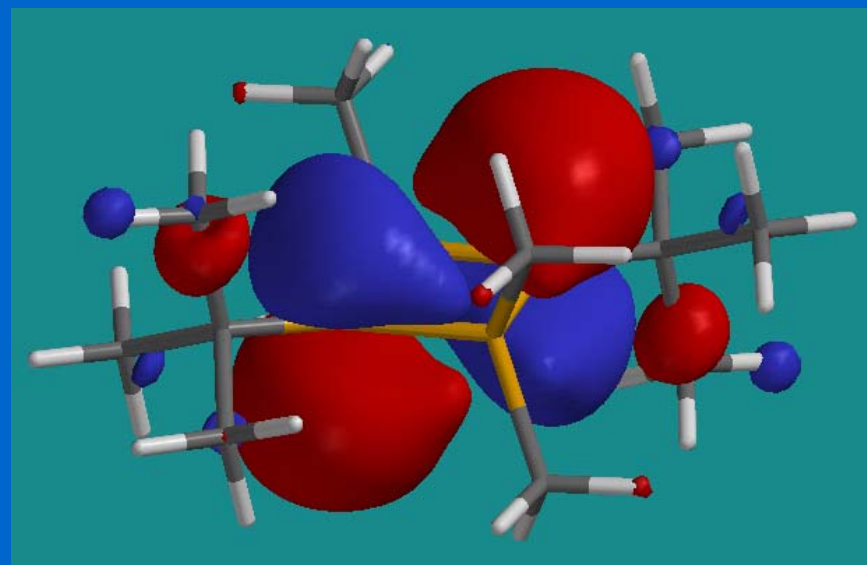
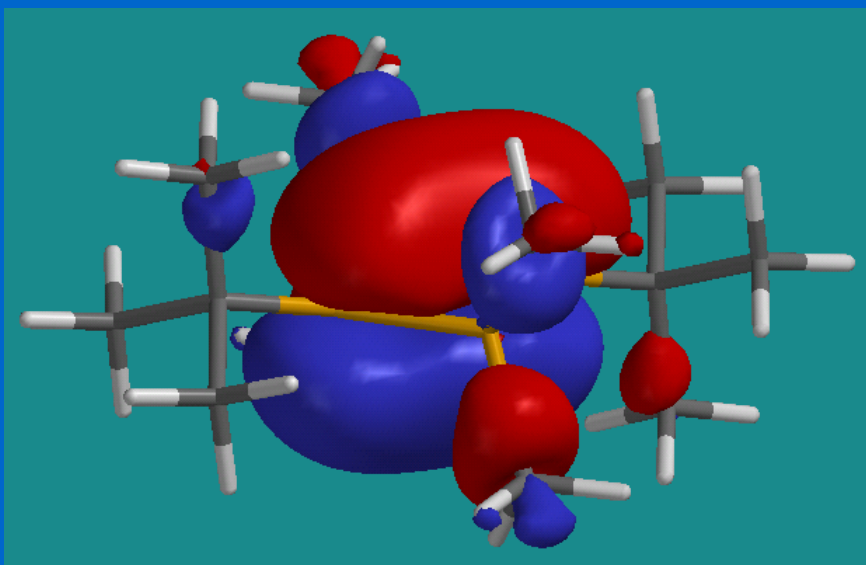


# *Challenges for wavefunction theory*

- Removing artificial computational scaling with size
  - “Local” correlation models
- Treating strong correlations tractably
  - Active space methods
  - Density matrix renormalization group
  - Reduced density matrix methods
- Overcoming very slow convergence with basis set
  - Incorporate 2-electron functions (of  $r_{12}$ )
  - Quantum Monte Carlo

# *New theories: strongly correlated electrons*

- Example: world's “first indefinitely stable singlet diradical”?
- HOMO: 1.83 electrons
- LUMO: 0.17 electrons



- Stability comes from reduced (17%) diradical character

## *Other general challenges*

- Linkages to theories at different length and time scales
  - Multiscale modeling
  - Dynamics & statistical mechanics
- Excited states and breakdowns of Born-Oppenheimer
  - Radiationless transitions, hot electrons
  - Conical intersections and photochemistry
- More physical insight
  - Not just a “numerical experiment”?

*Our most exciting days are ahead of us...*



Og discovered fire, and Thorak invented the wheel.  
There's nothing left for us.

# *Question 1*

## *Question 2*



## *Question 3*