Finite Element Analysis of Rydberg States

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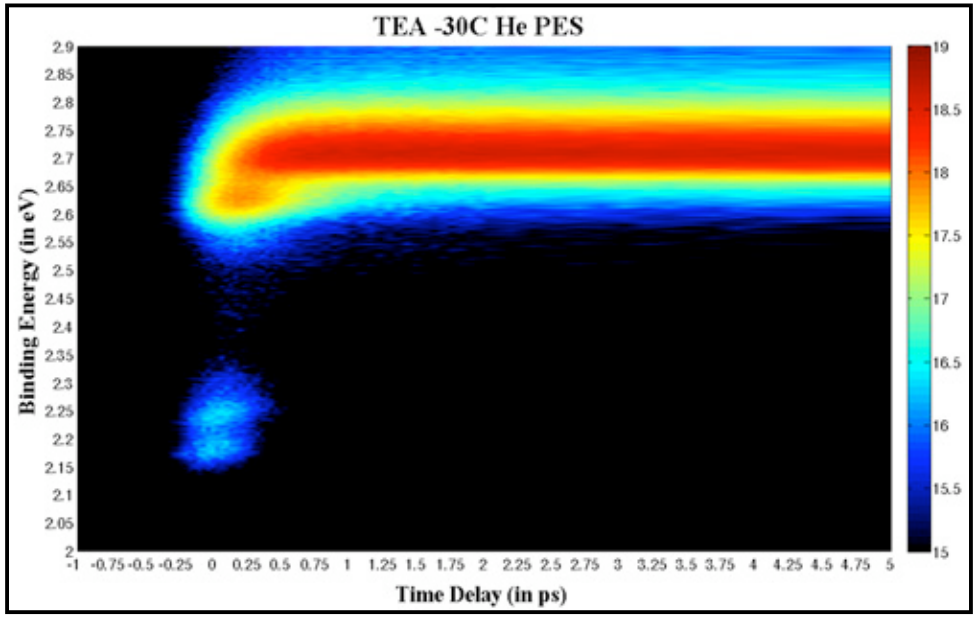
Funding

•Army Research Office

•Department of Energy

Challenge: Ultrafast Structural Dynamics

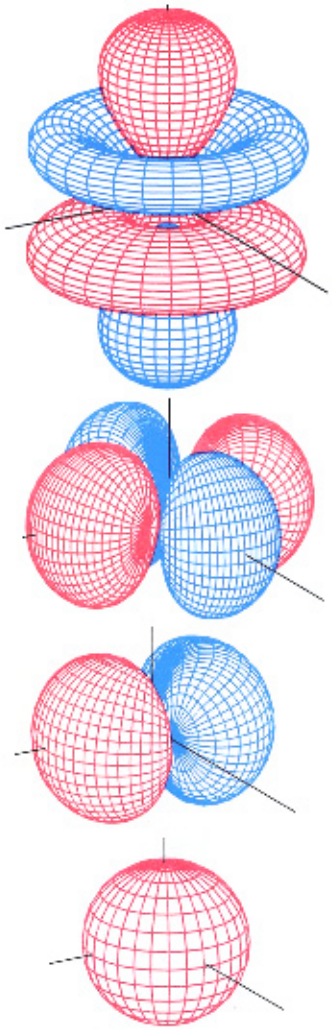
- Observe molecules while they do chemistry
- Requires <100 fs (10^{-15} s) time resolution
- Requires new spectroscopic tools



Recent Discovery:

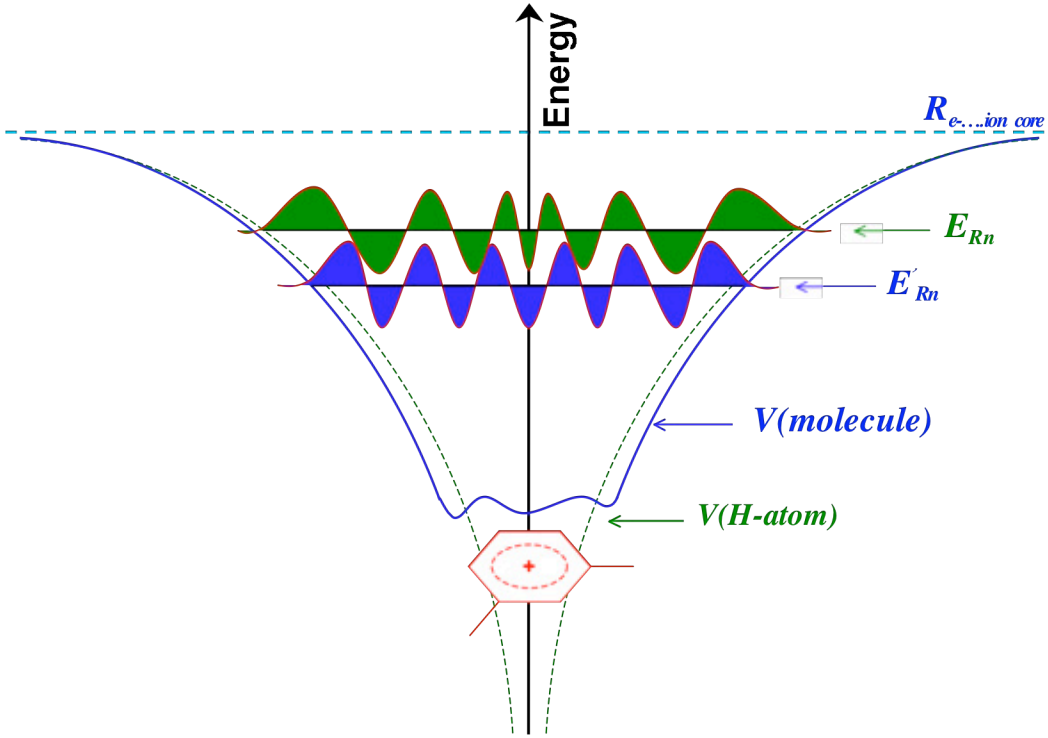
- Rydberg specta encode molecular structure
- Technology developed to measure with fs time resolution
- Needed: Computational link spectrum ⟺ structure

Quantum Mechanics of Rydberg States



$$-\frac{\hbar^2}{2m}\nabla^2 u + Vu = \lambda u$$

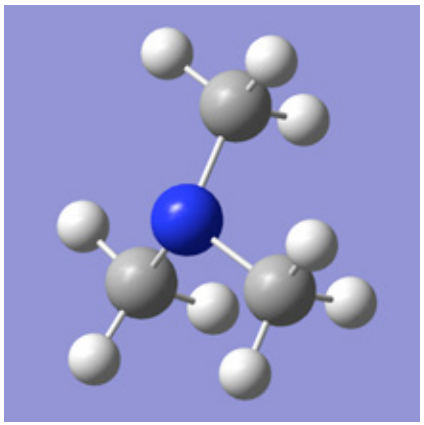
Schrödinger equation

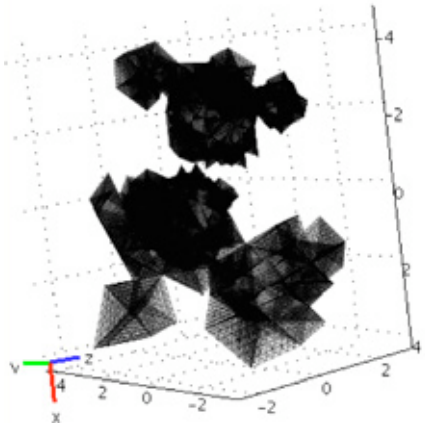


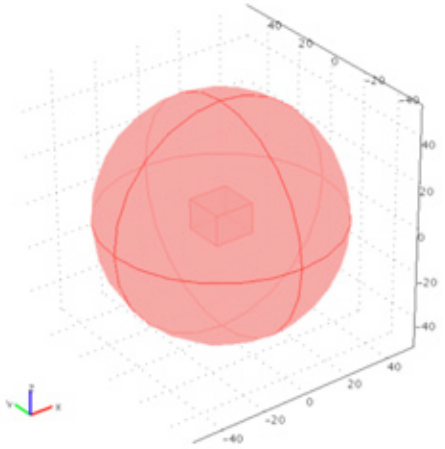
Calculation Scheme

$$-\frac{\hbar^2}{2m}\nabla^2 u + Vu = \lambda u$$

Molecular Geometry ⇨ GAUSSIAN ‘03 ⇨ Potential ⇨ COMSOL

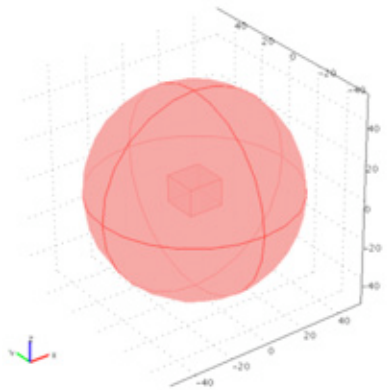






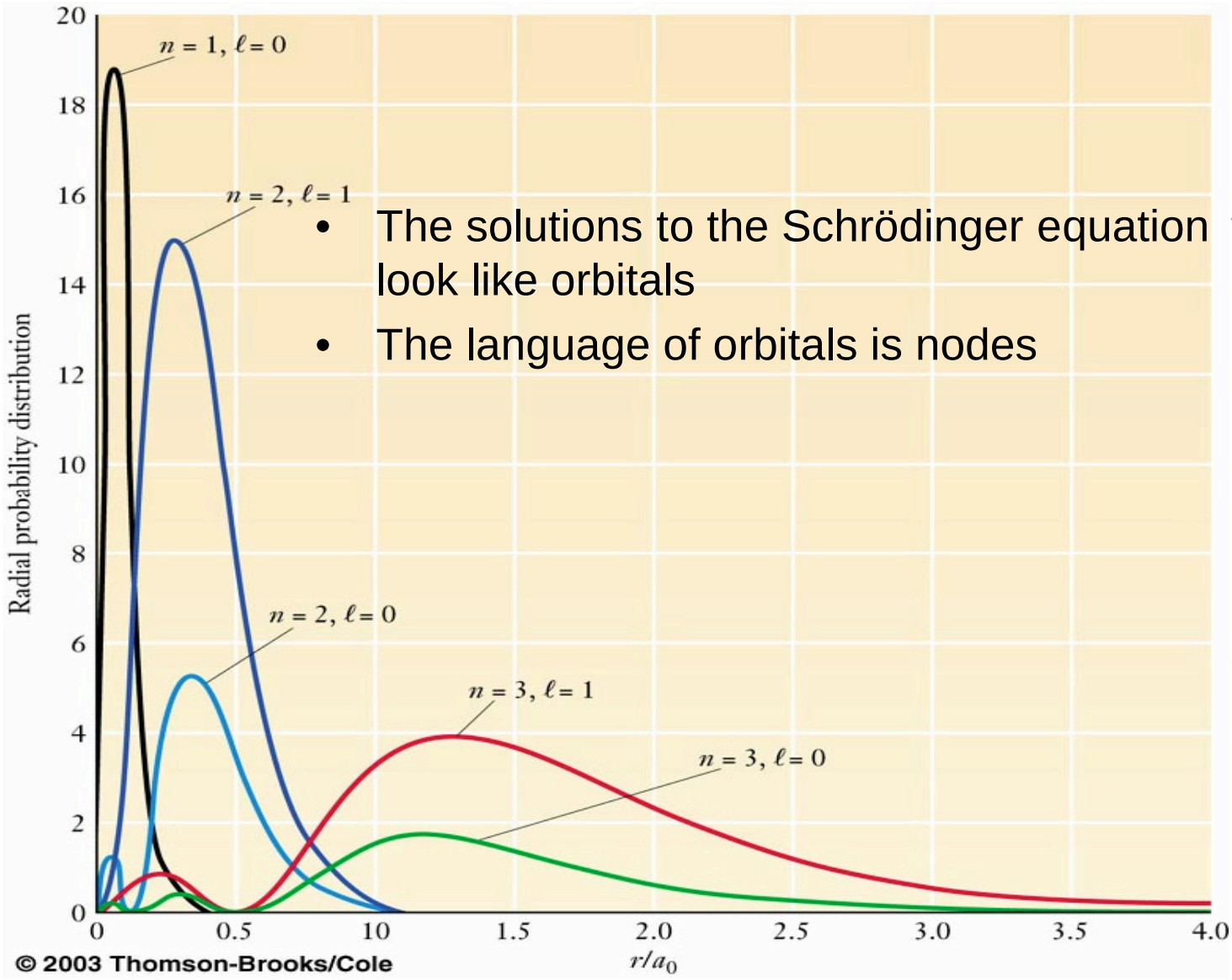
Inside COMSOL

$$-\frac{\hbar^2}{2m}\nabla^2 u + Vu = \lambda u$$

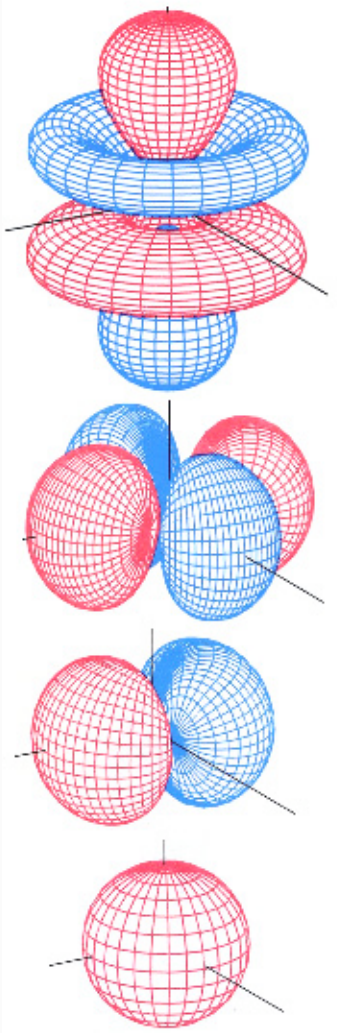


- *PARDISO solver*
- *20 eigenvalues around expected value*
- *Dirichlet Boundary Condition*
- *Matrices set to Hermitian*
- *Fine Potential Resolution in Inner Cube*
- *Coarser Potential Resolution Outside*
- *Mesh Density Proportional to Potential Resolution*

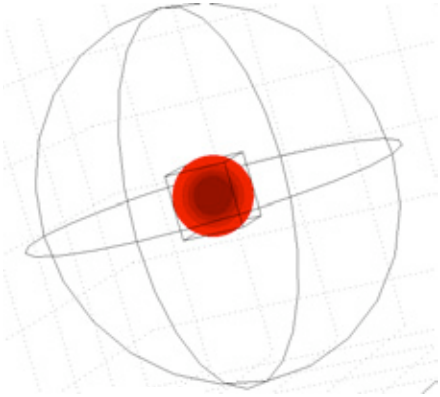
Orbitals



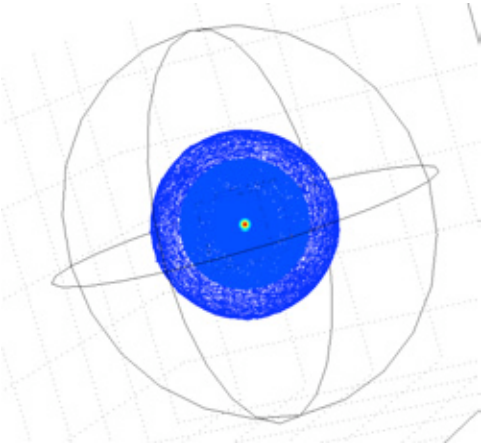
- The solutions to the Schrödinger equation look like orbitals
- The language of orbitals is nodes



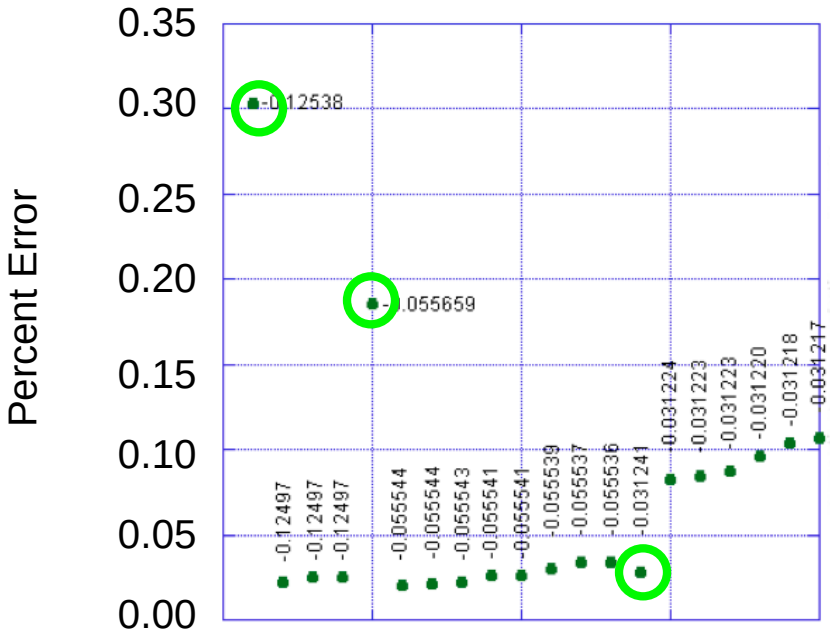
Hydrogen in Cartesian Coordinates



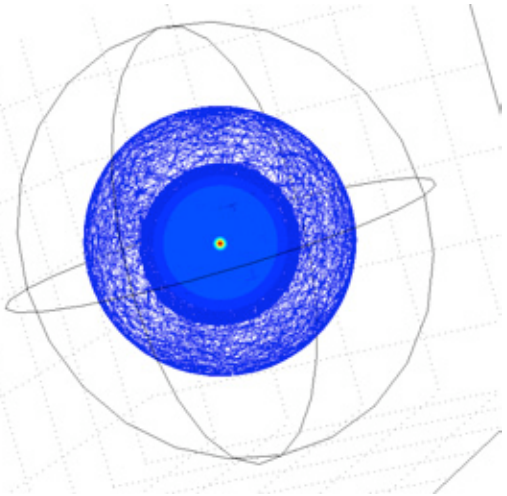
$\sqrt{\langle r^2 \rangle}$ = 6.46 au



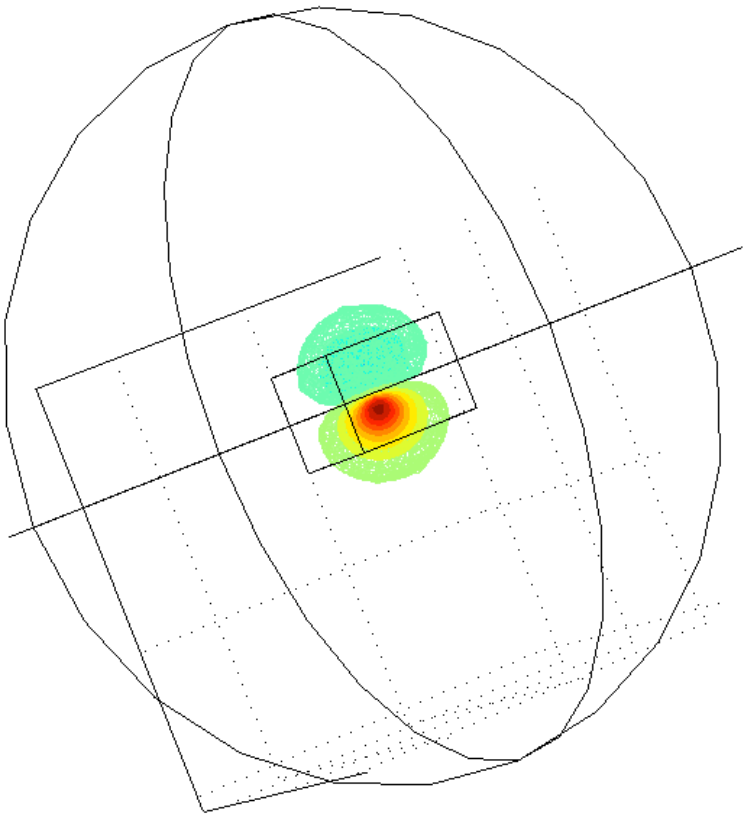
$\sqrt{\langle r^2 \rangle}$ = 14.36 au

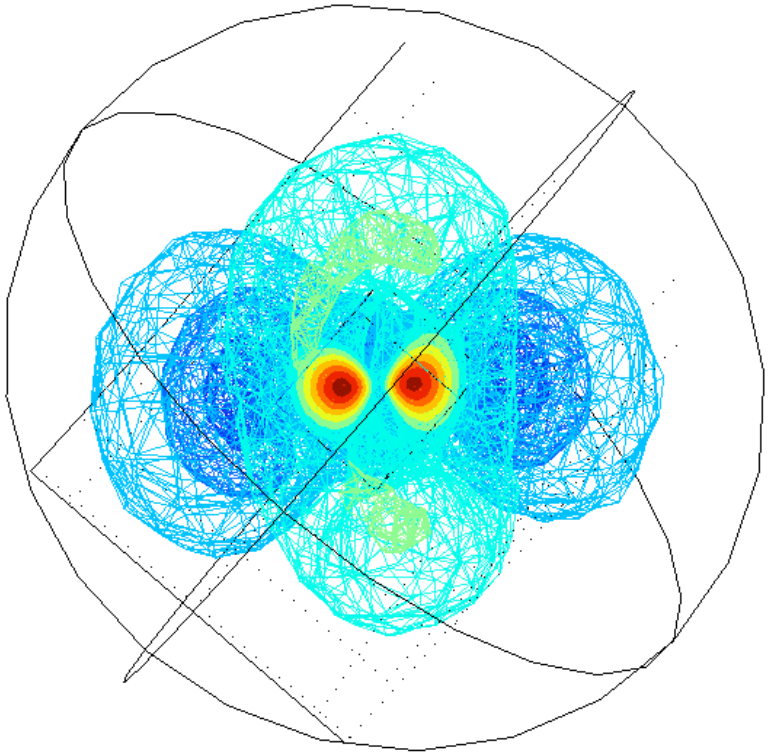


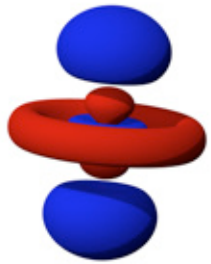
$\sqrt{\langle r^2 \rangle}$ = 25.14 au



Hydrogen Interpolated Solution

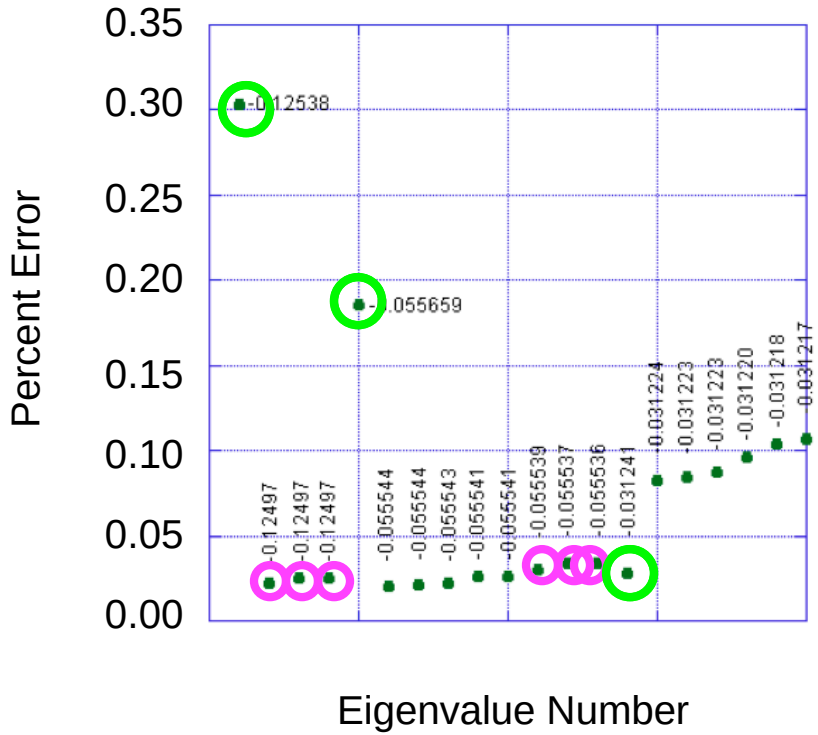




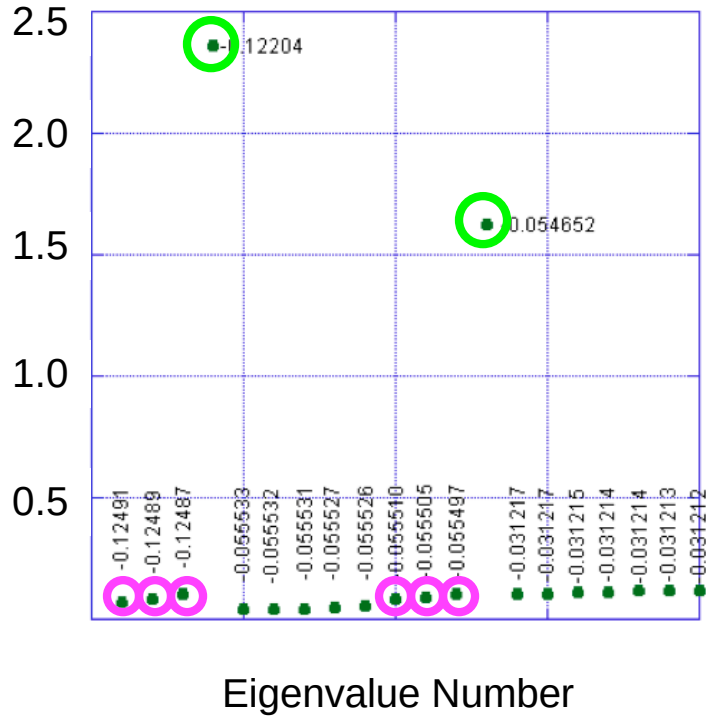


Hydrogen in Cartesian Coordinates

Using analytical potential



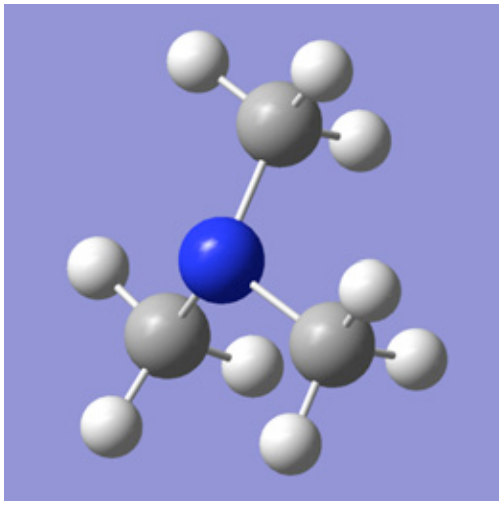
Using imported potential

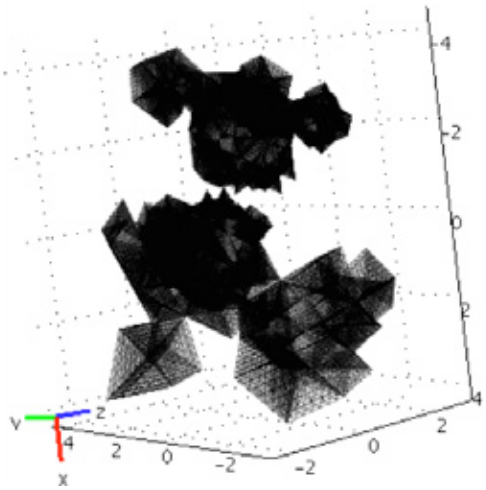


Conclude:

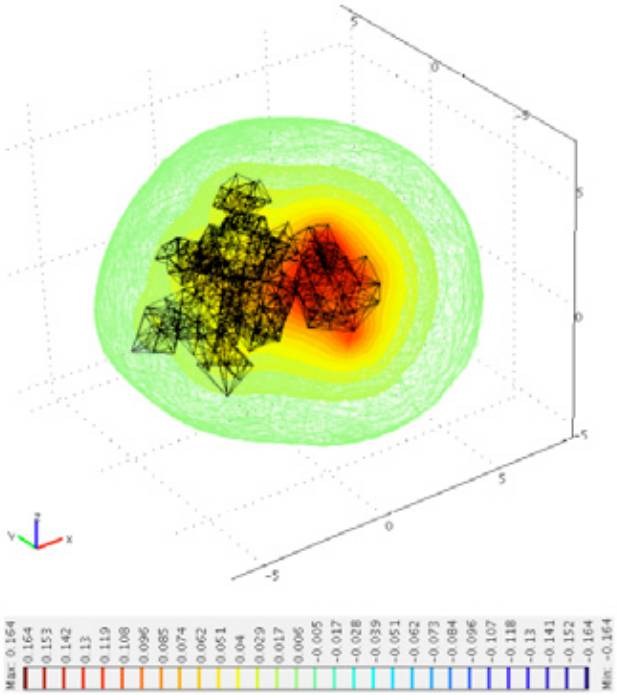
- Errors are in the 1% range for s orbitals using interpolated potentials
- For higher angular momentum states, errors remain ≤ .1 %

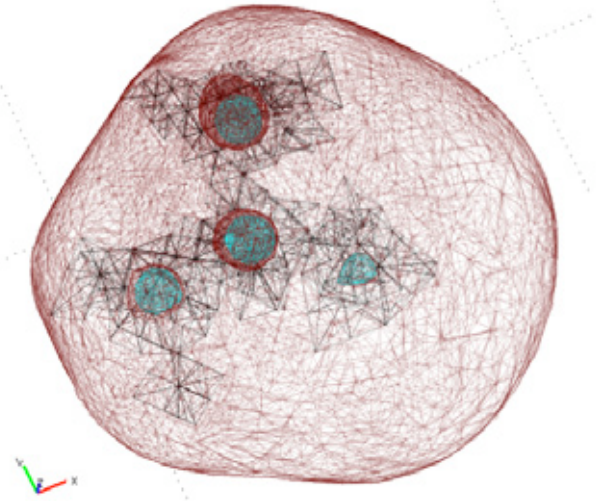
Trimethylamine (TMA) - Introduction





3s Eigenvalue





$\sqrt{\langle r^2 \rangle}$ = 3.92 au

$E_{\text{This work}}$ = -3.323 eV

$E_{\text{Experiment}}$ = -3.087 eV % error = 7.6%

$E_{\text{Previous ab initio}}$ = -3.202 eV % error = 3.4%

3p Eigenvalue

$E_{\text{this work}}$ = -2.217 eV

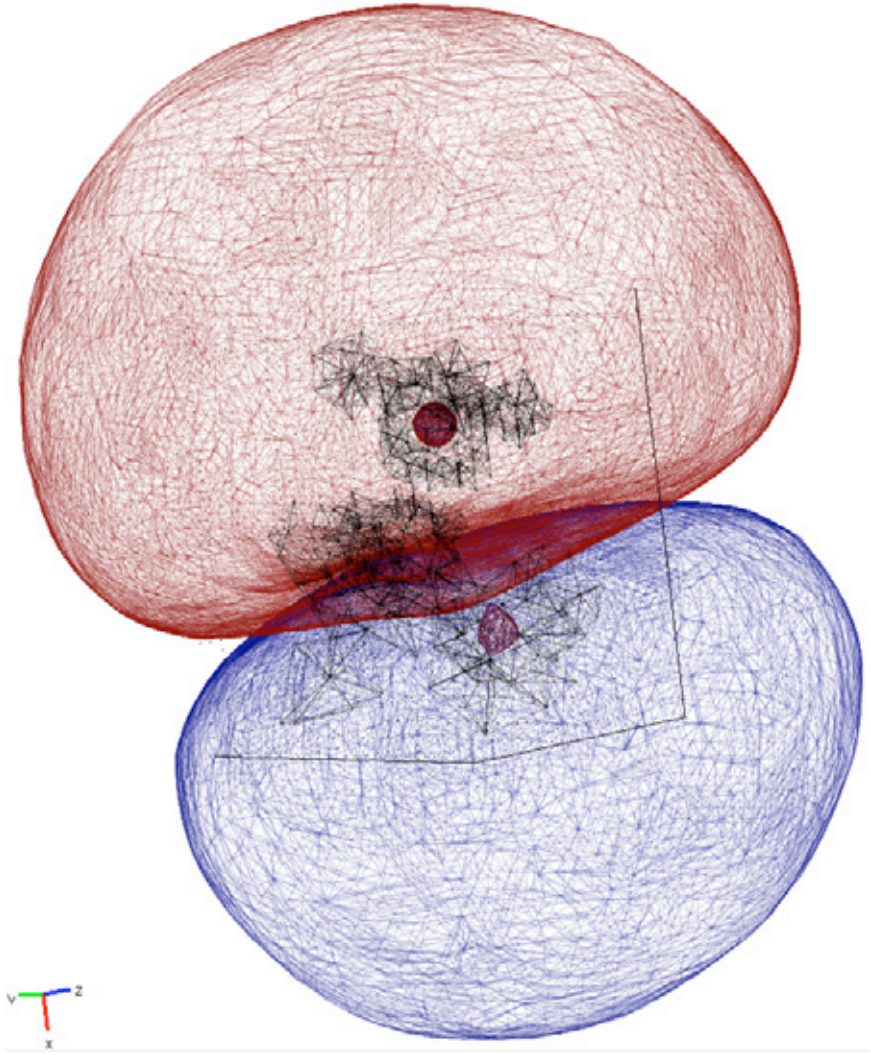
$E_{x,y\,\text{experiment}}$ = -2.251 eV %$_{\text{error}}$ = 1.5%

$E_{z\,\text{experiment}}$ = -2.204 eV %$_{\text{error}}$ = 0.6%

$E_{x,y\,\text{ab initio}}$ = -2.517 eV %$_{\text{error}}$ = 12 %

$E_{z\,\text{ab initio}}$ = -2.317 eV %$_{\text{error}}$ = 6.4%

$\sqrt{\langle r^2 \rangle}$ = 4.038 au

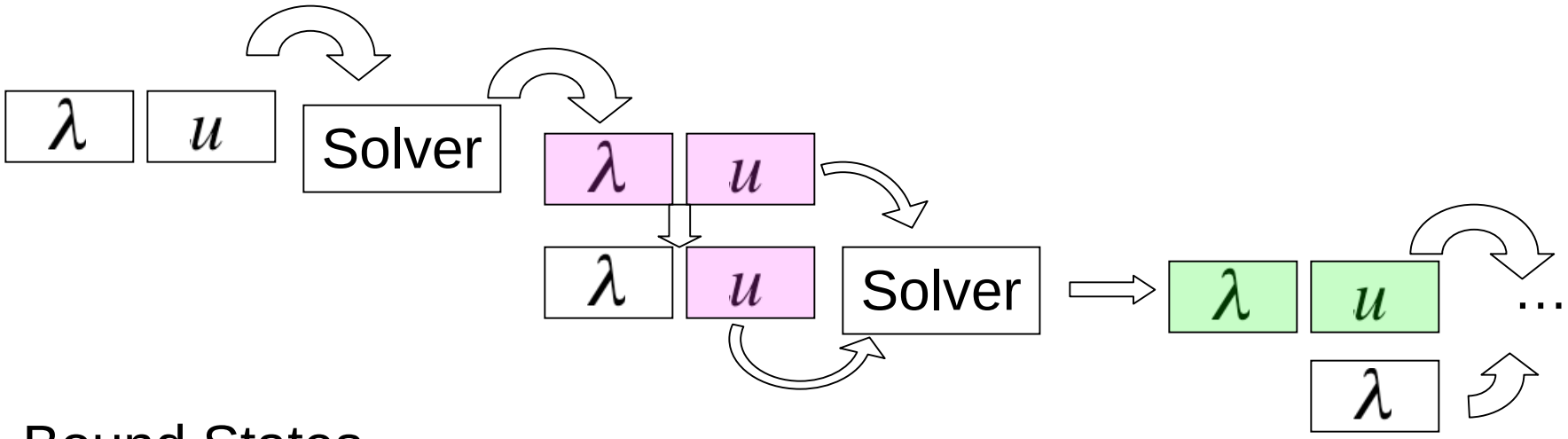


TMA - Conclusion

- We have demonstrated a new conceptual approach to calculate Rydberg orbitals
- We have calculated the most accurate TMA 3p eigenvalue ever.
- Our method shows promise of scaling well for eigenvalue computation of large molecules, opening up new venues of computation.

Algorithmic Issues

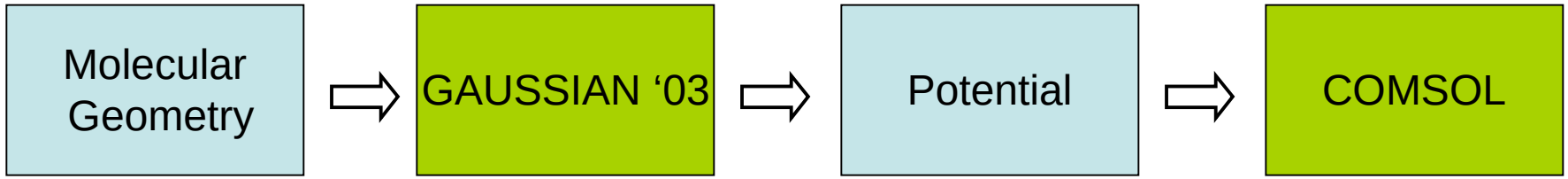
Initial Conditions



Bound States

Or, how can I bias the solver to return only negative eigenvalues?

Next Steps



- Choose new molecules
- Examine different conformations of the molecules

- Examine the effects of different basis sets

- Deal with issues from truncating the negative infinity

- Improve algorithm
- Further optimize mesh
- Fully explore all eigenvalues of the molecules

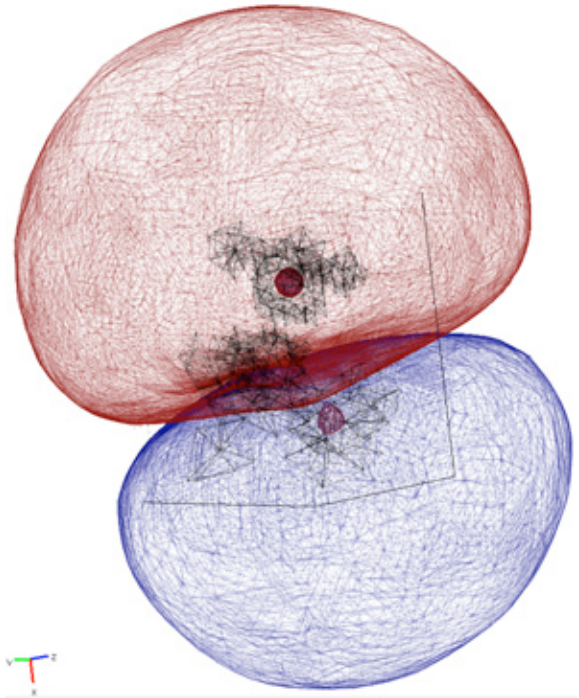
Theory

- Use method to explain new chemistry

Thank You!

COMSOL CONFERENCE 2009

OCTOBER 8-10 2009, BOSTON, MA, USA



Any Questions? Comments? Ideas?