JÜLICH
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Self-consistent atomic orbital computation and visualization

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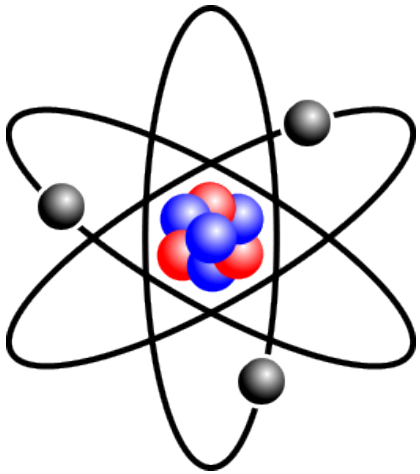
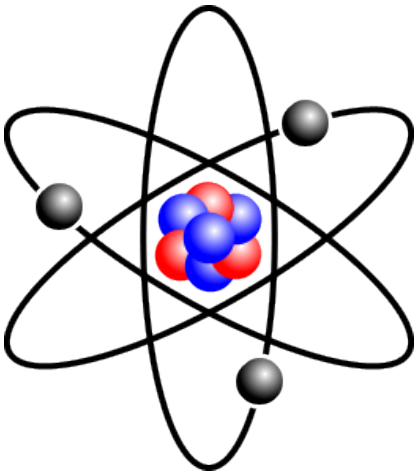
Jülich Supercomputing Center German Research School for Simulation Sciences

Outline

Introduction



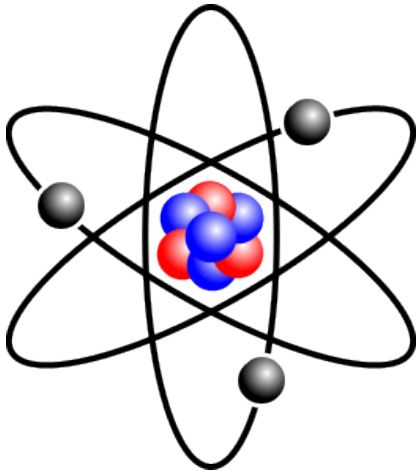
Introduction



Question:

How do the electrons distribute around the nucleus?

Introduction



Question:

How do the electrons distribute around the nucleus?

Answer:

Solve the Schrödinger equation:

$$H\psi = E\psi$$

where

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_i} \right] + \sum_{i<j} \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Objectives

1. Solve the simplest case: one-electron system
2. Approximate the general case: many-electron system
3. Monte-Carlo sampling to visualize obtained atomic orbitals

One-electron system

For $N = 1$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \right] \psi = E\psi$$

Separation of variables:

$$\psi(r, \theta, \phi) = R(r)\,Y(\theta, \phi)$$

Angular part	$Y(\theta, \phi)$	Easy, spherical harmonics
Radial part	$R(r)$	Difficult, our task

One-electron system

Define $u(r) \equiv rR(r)$, radial equation

$$\boxed{-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left[-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]u = Eu}$$

Employ atomic units

$$\hbar = 1 \quad m_e = 1 \quad e = 1 \quad 4\pi\epsilon_0 = 1$$

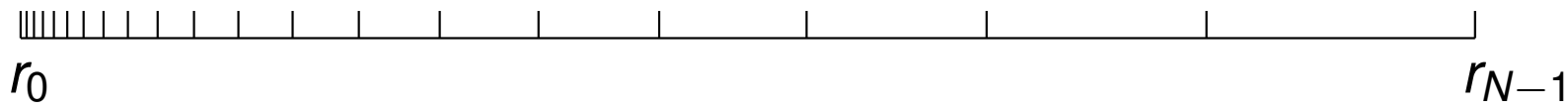
We have

$$-\frac{1}{2}\frac{d^2u}{dr^2} + \left[-\frac{Z}{r} + \frac{1}{2}\frac{l(l+1)}{r^2}\right]u = Eu$$

Numerical method

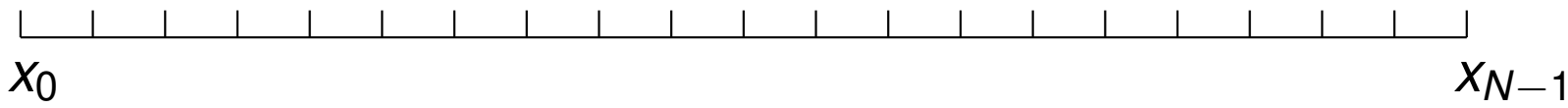
Construct a logarithmic grid $0 < r_0 < \cdots < r_{N-1} < \infty$, where

$$r_i = \frac{1}{Z} e^{x_i}$$



where x is a uniformly distributed grid

$$x_i = x_0 + i\Delta x$$



Numerical method

Transform non-uniform grid r to uniform grid x
Introducing $\tilde{u} \equiv u/\sqrt{r}$

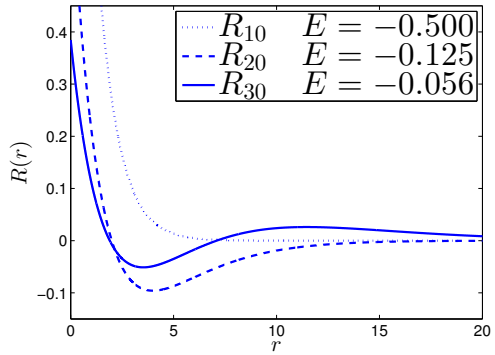
$$-\frac{1}{2}\frac{d^2\tilde{u}}{dx^2} + \left[-rZ + \frac{1}{2}\left(l+\frac{1}{2}\right)^2\right]\tilde{u} = r^2 E\tilde{u}$$

Finite-difference $\frac{d^2\tilde{u}}{dx^2} \approx \frac{\tilde{u}_{i+1}-2\tilde{u}_i+\tilde{u}_{i-1}}{\Delta x^2}$, we obtain

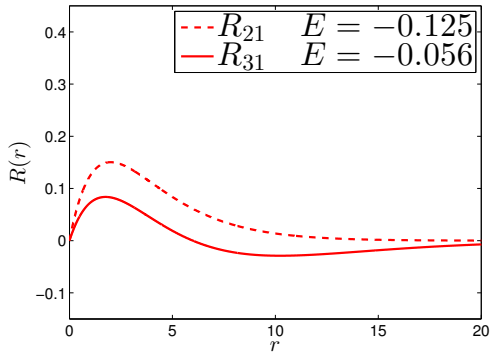
$$\tilde{u}_{i+1} = \left\{2 + 2\Delta x^2\left[-r_i Z + \frac{1}{2}\left(l+\frac{1}{2}\right)^2 - r_i^2 E\right]\right\}\tilde{u}_i - \tilde{u}_{i-1}$$

This is a simple recursion!

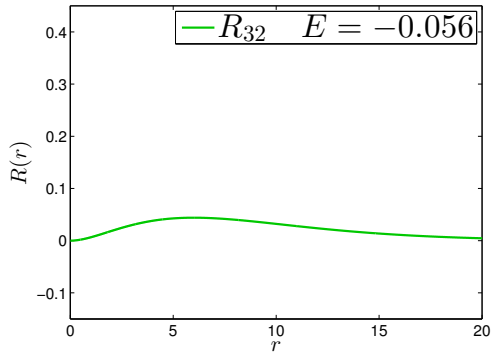
Numerical results



(a) R_{10}, R_{20} and R_{30}



(b) R_{21} and R_{31}



(c) R_{32}

Figure: Numerical results of the first few radial wave functions, $R_{nl}(r)$

Many-electron system

Many-electron Schrödinger equation

$$\left\{ \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right\} \psi = E\psi$$

- This equation cannot be solved exactly
- We use self-consistent field (SCF) approximation

Many-electron system

The exact Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + \underbrace{\sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{trouble maker}}$$

is approximated by

$$H_0 = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + V_H(r)$$

where $V_H(r)$ is called the Hartree potential

Many-electron system

The many-electron problem breaks down to multiple one-electron problems

$$\left\{\left[-\frac{\hbar^2}{2m_e}\nabla^2-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right]+V_H(r)\right\}\psi_i=E_i\psi_i$$

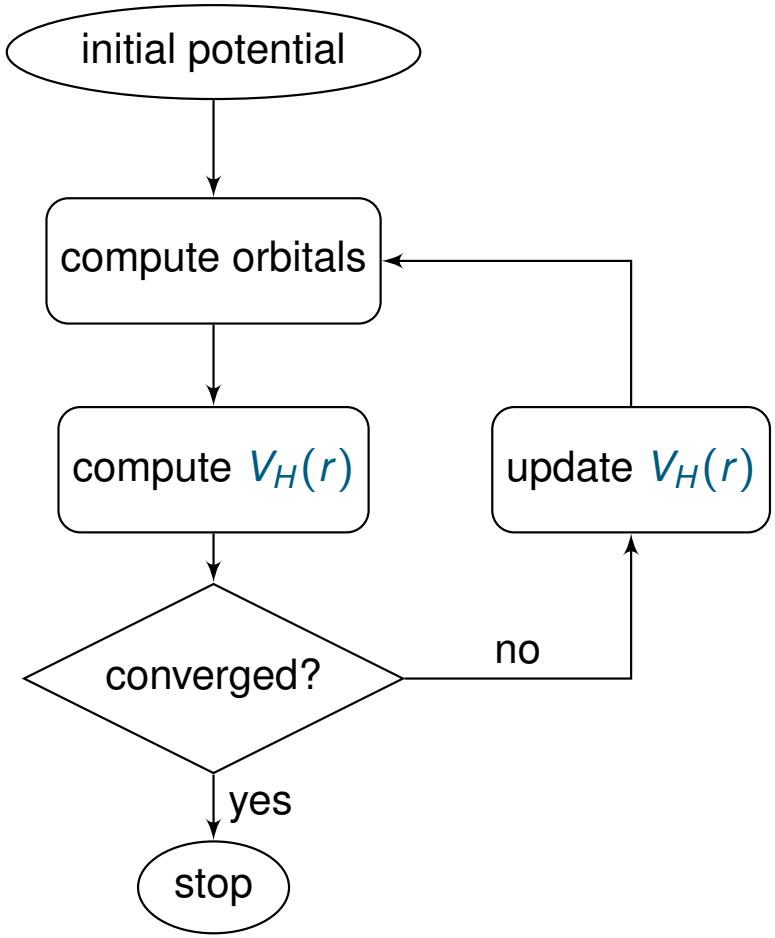
The radial equation

$$\boxed{-\frac{\hbar^2}{2m_e}\frac{d^2u_i}{dr^2}+\left[-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}+\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}+V_H(r)\right]u_i=E_iu_i}$$

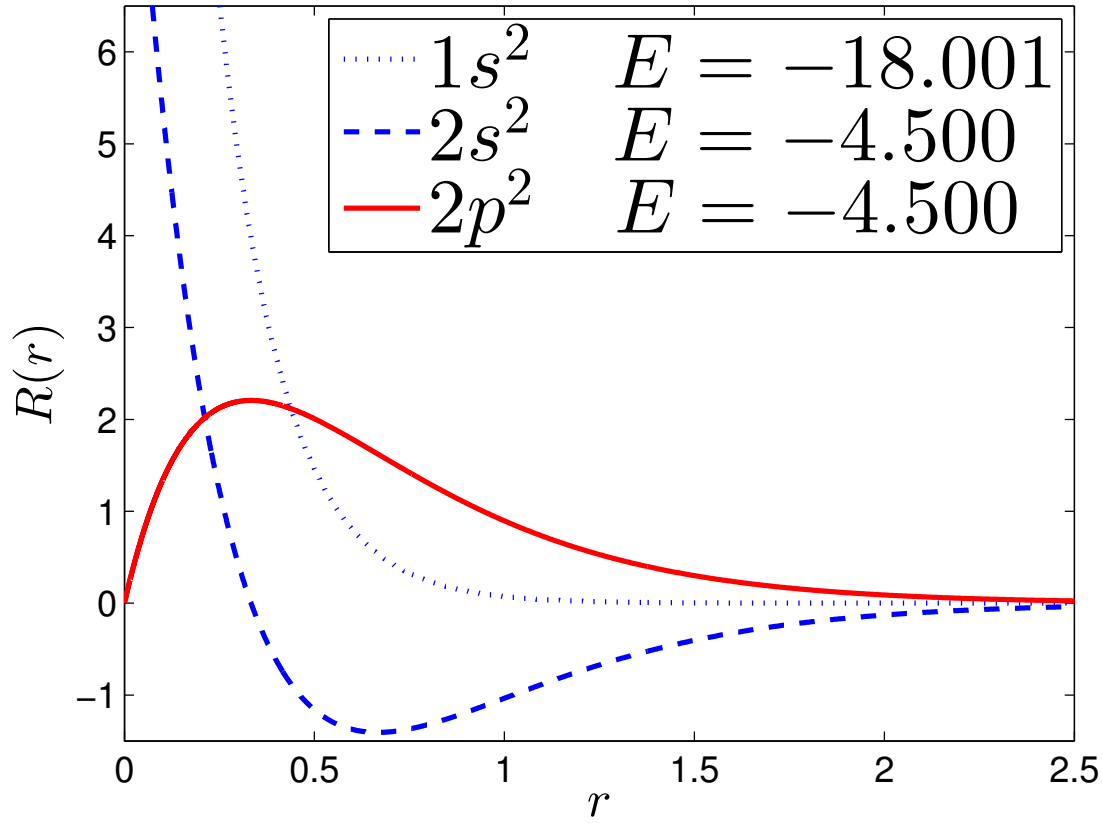
But, what is $V_H(r)$?

Self-consistent approximation

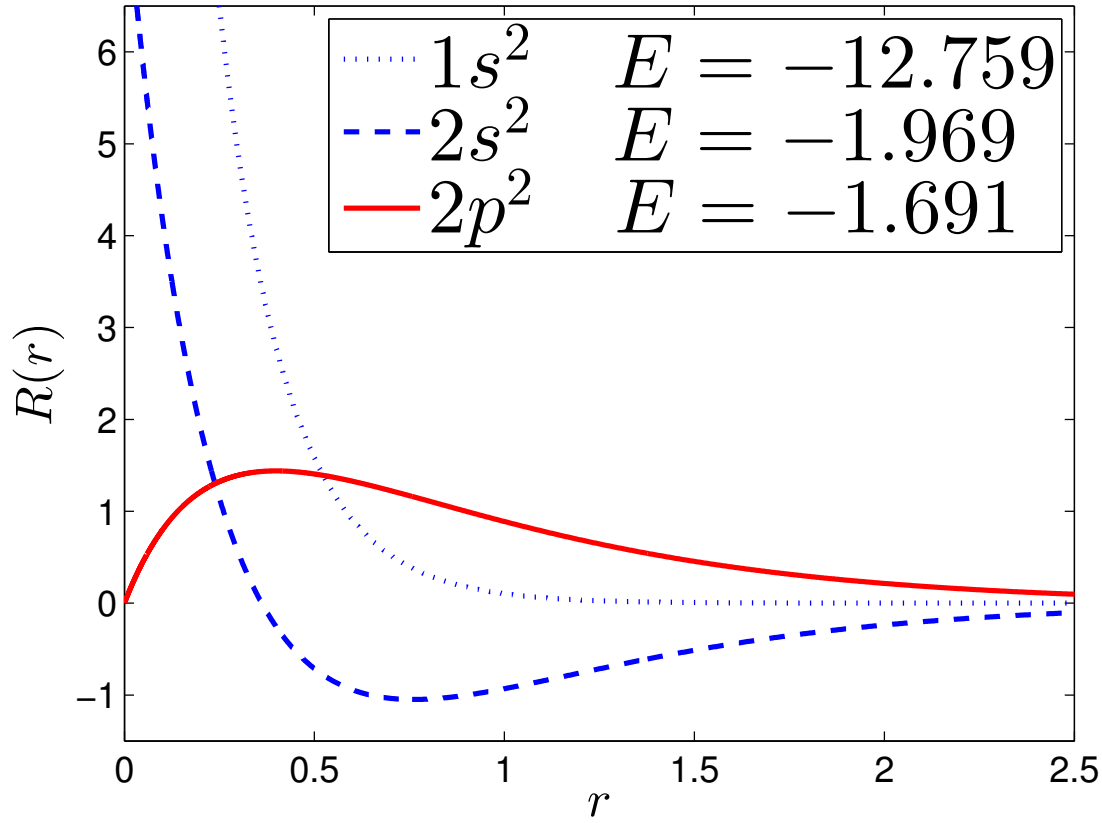
- $V_H(r)$ is the mean-field potential created by all electrons
- If we roughly know where the electrons are, we know $V_H(r)$
- This implies an iteration scheme



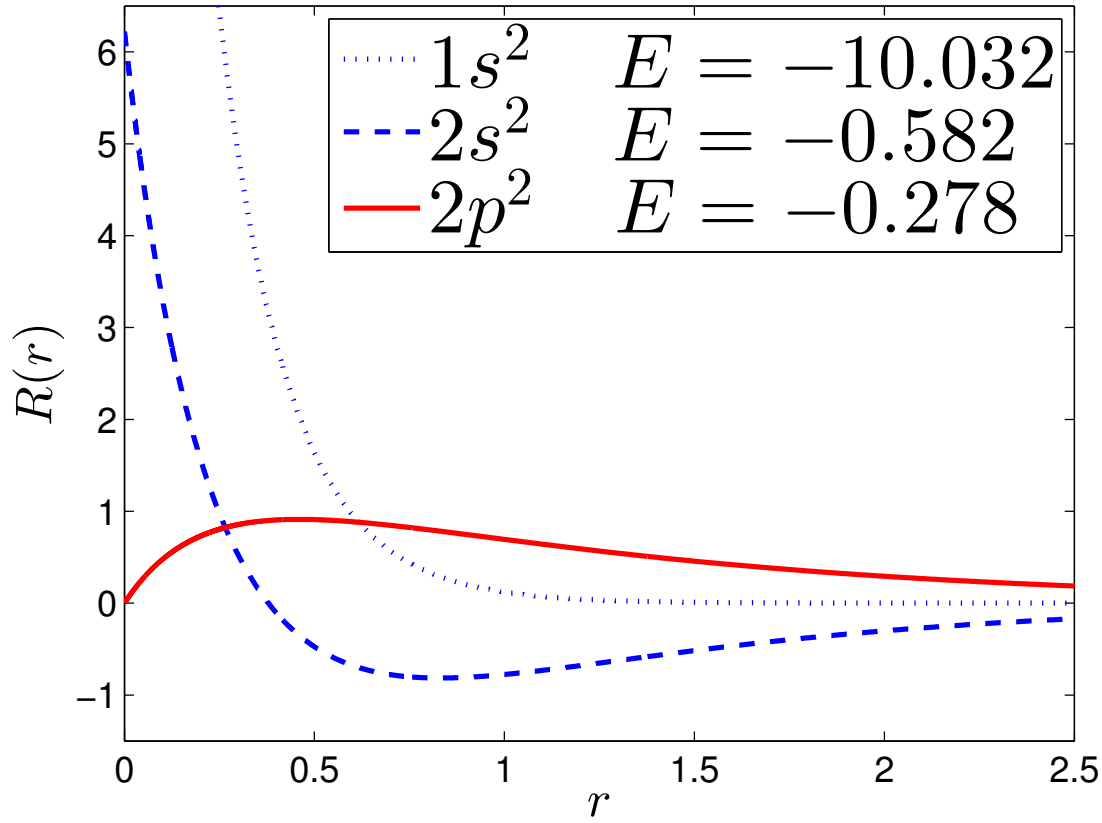
Carbon: 6 electrons (Iteration = 1)



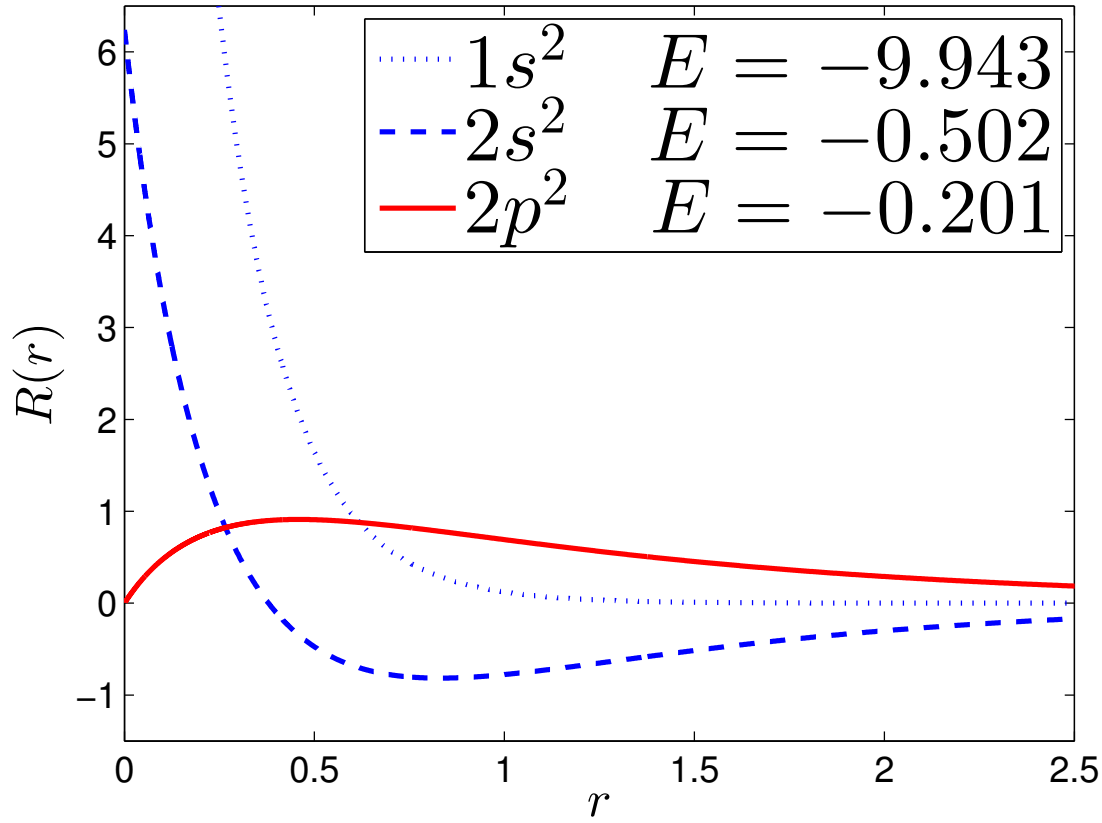
Carbon: 6 electrons (Iteration = 2)



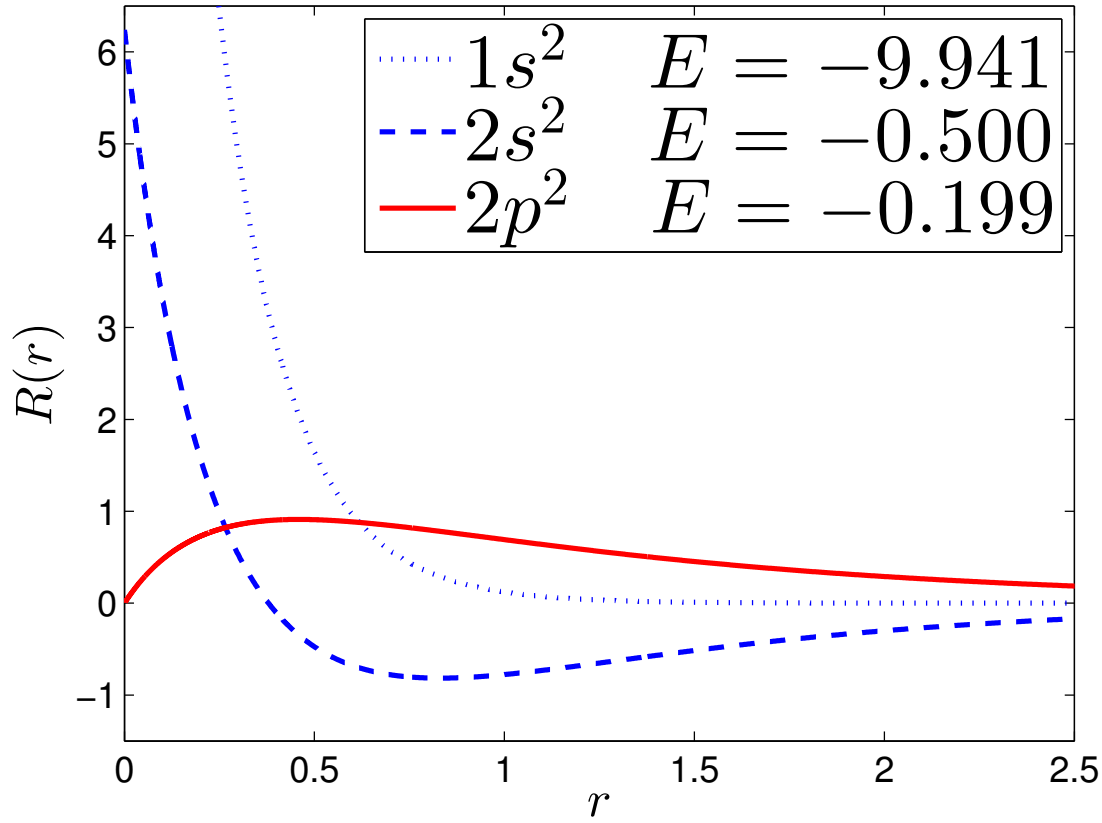
Carbon: 6 electrons (Iteration = 5)



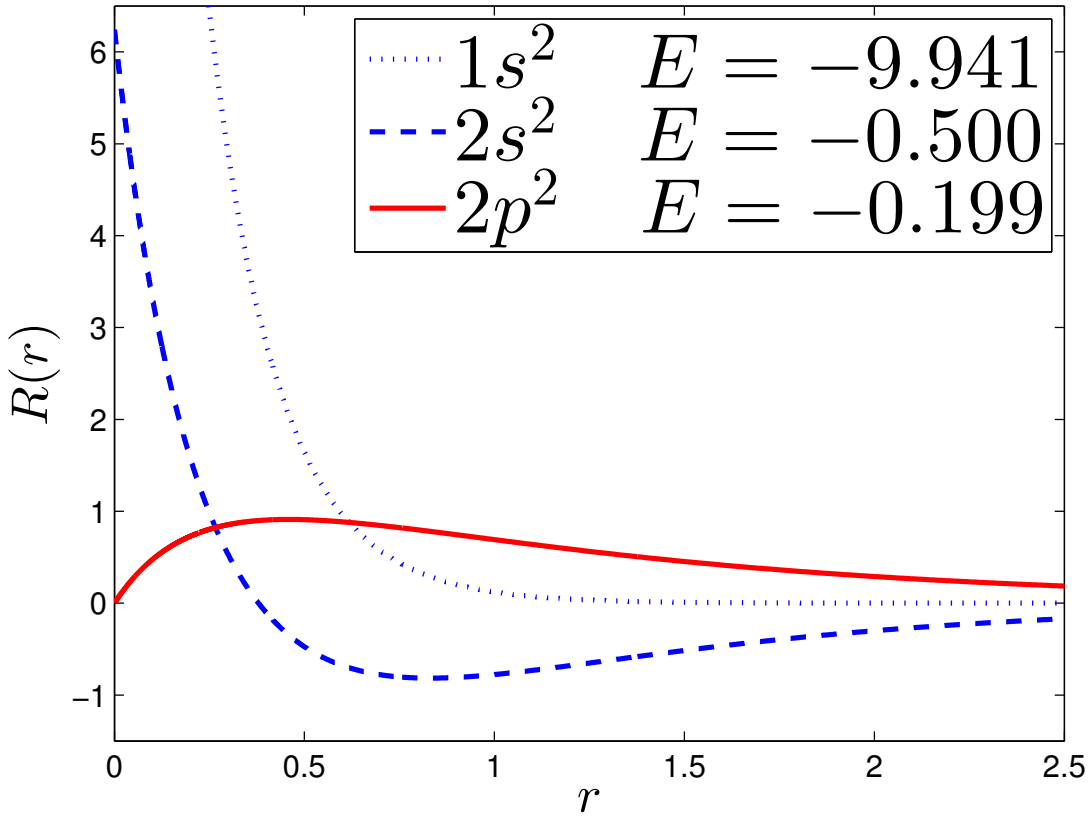
Carbon: 6 electrons (Iteration = 10)



Carbon: 6 electrons (Iteration = 15)

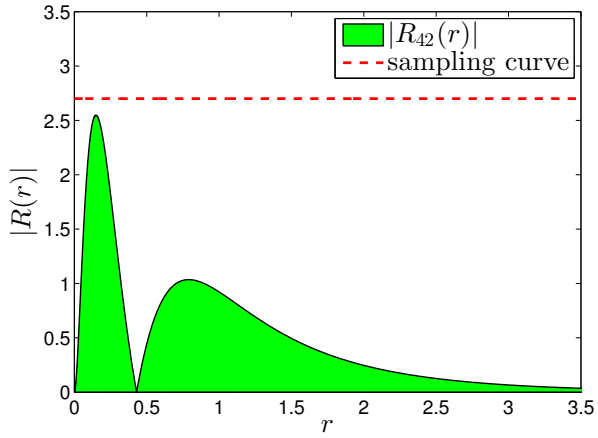


Carbon: 6 electrons (Iteration = 20)

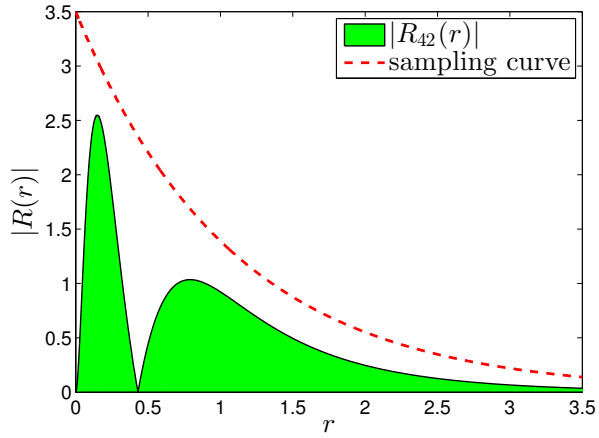


Atomic orbital visualization

- $\psi(r, \theta, \phi)$ is a 4D object lives in 3D space, difficult to visualize!
- We perform Monte-Carlo sampling to visualize $\psi(r, \theta, \phi)$ in a probabilistic approach



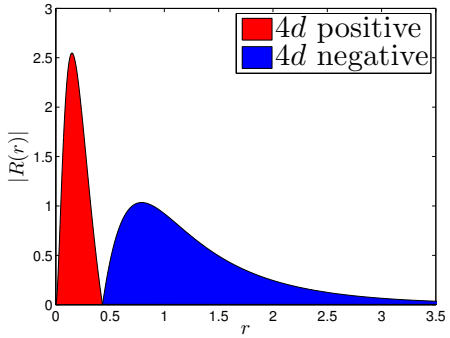
Inefficient

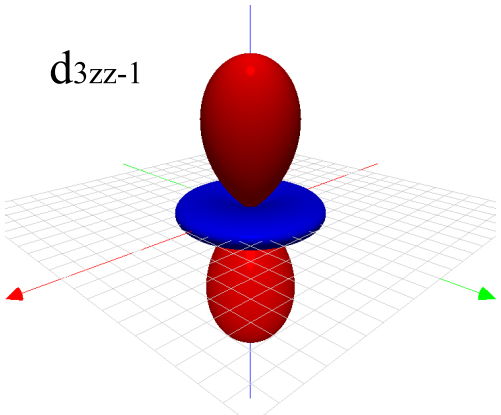


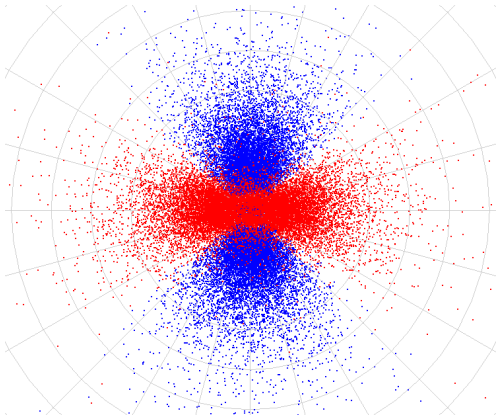
Efficient!

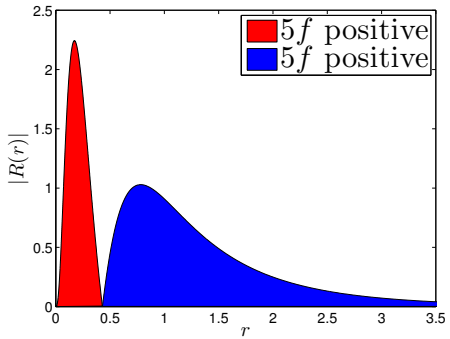
Atomic orbital visualization

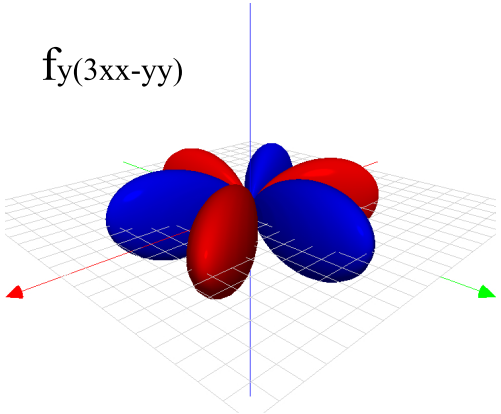
Radial part × Angular part = Atomic orbital

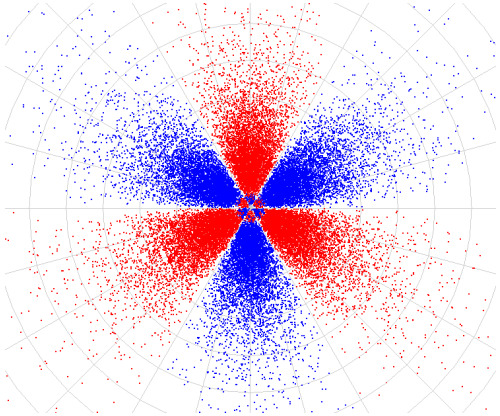












Conclusion

1. Starting from the simplest case, we computed the atomic orbitals for the one-electron system
2. By self-consistent field approximation, we obtained the atomic orbitals for the many-electron system
3. Using weighted Monte-Carlo sampling, we successfully visualized the atomic orbitals

Thank You!

I am heartily thankful to:

- My supervisor, Prof. Dr. Erik Koch
- Jülich Supercomputing Center
- German Research School for Simulation Sciences