Solving the Helium Atom

or: *Why Chemistry Exists.*

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Quantum Physics

- Particles are described by complex-valued "wavefunctions" $\psi \quad |\psi\rangle$
- Amplitude squared is probability $P(x) = \psi^*(x)\psi(x) = \langle\psi|\hat{x}|\psi\rangle$
- Wavefunctions contain all possible information
- "Operators" act on wavefunctions
  - Hamiltonian to get energy, etc

$$\langle E\rangle = \langle\psi|\hat{H}|\psi\rangle$$

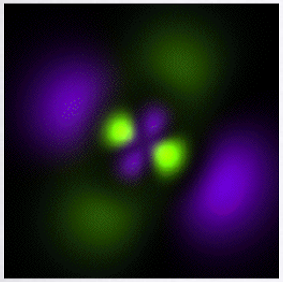
$$\hat{p}_x|p\rangle = p|p\rangle$$

- Schrödinger equation: non-relativistic particles

$$\hat{H}(t)|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle \qquad \left[-\frac{\hbar}{2m}\nabla^2 + V(r)\right]\psi(r) = E\psi(r)$$

Why helium is hard

- Hydrogenic atoms (one electron) can be solved exactly



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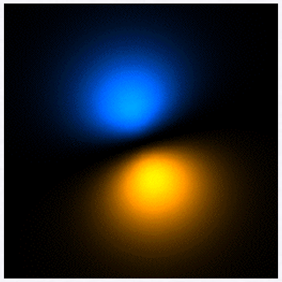

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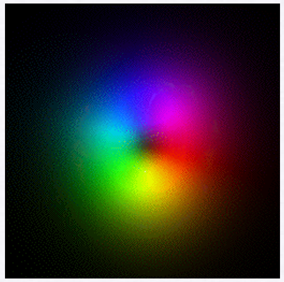

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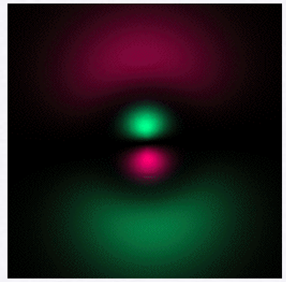


|3,1,0>

- But multiple electrons means interactions

- Interactions means we’re screwed

  - Three-body problem

$$< 1|V|1 >= \int_0^\infty r_1^2 dr_1 \int_0^\pi \sin\vartheta_1 d\vartheta_1 \int_0^{2\pi} d\varphi_1$$

$$\left\{ e^{-\alpha r_1}\frac{1}{r_1}\left(\sum_{n=0}^{\infty} \frac{\prod_{i=0}^{n-1}(2i+1)}{n!}\frac{\left(\frac{r_2}{r_1}\right)^n(\cos\vartheta_1\cos\vartheta_2+\sin\vartheta_2\sin\vartheta_1\cos(\phi_2-\phi_1))^n}{(1+\left(\frac{r_2}{r_1}\right)^2)^{\frac{2n+1}{2}}}\right)e^{-\alpha r_1}\right\}$$

Hartree-Fock Approximation

- Electrons are indistinguishable, so one wavefunction
- H-F: approximate the electrons as separate particles, one the external potential for the other
- Repeatedly calculate R(r) and V(R(r)) until stuff converges
- “Self consistent field approximation”

Equations

- For helium, we can assume spherical symmetry

$$\psi(x) = \frac{1}{(4\pi)^{1/2} r} R(r) \left| \pm \frac{1}{2} \right\rangle$$ Single particle wavefunction

$$\psi(x) = \frac{1}{\sqrt{2}} \frac{1}{4\pi r_1 r_2} R_1(r) R_2(r) \left[\left| +\frac{1}{2} \right\rangle_1 \left| -\frac{1}{2} \right\rangle_2 - \left| -\frac{1}{2} \right\rangle_1 \left| +\frac{1}{2} \right\rangle_2 \right]$$ Two particle

$$E = \frac{\hbar^2}{m} \int_0^\infty \left(\frac{dR}{dr} \right)^2 dr + \int_0^\infty \left[-\frac{Ze^2}{r} + \frac{1}{4} \Phi(r) \right] \rho(r) 4\pi r^2 dr$$ Energy

$$\int_0^\infty R^2(r) dr = 1 \qquad \rho(r) = \frac{1}{2\pi r^2} R^2(r) \qquad \int_0^\infty \rho(r) 4\pi r^2 dr = 2$$

More Equations

- Use calculus of variations and Lagrange multipliers on Energy equation to get:

$$\left[-\frac{\hbar}{2m}\frac{d^2}{dr^2}-\frac{Ze^2}{r}+\frac{1}{2}\Phi(r)-\varepsilon\right]R(r)=0$$

- This is the first equation we solve, to get R(r).

- To get V, we solve:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Phi}{dr}\right)=-4\pi e^2\rho$$

Simplify this to avoid the singularity

$$\frac{d^2\phi}{dr^2}=-4\pi e^2 r\rho$$

$$\Phi(r)=r^{-1}\phi(r)$$

Methods

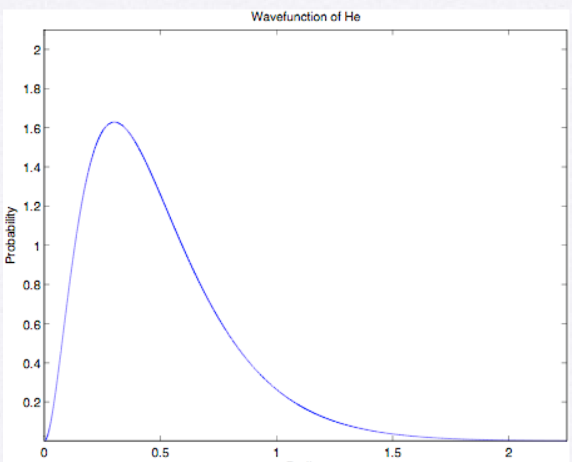
- Originally tried shooting method & Mathematica
- Switched to finite differences & Matlab
- Penta-diagonal matrix, but with 5 elements in first two and last two rows, NxN, solving to some radius L

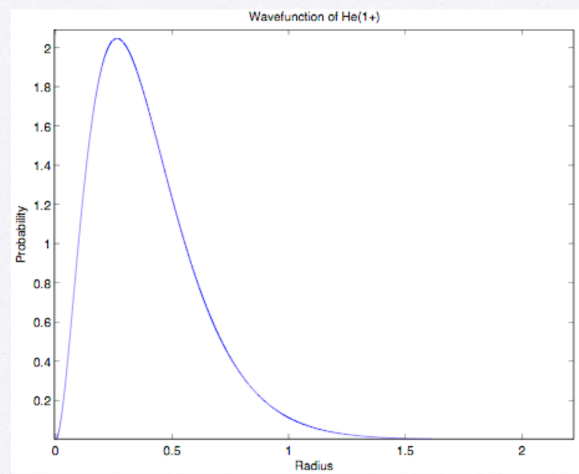
$$\begin{matrix}
X & X & X & X & X & & & \\
X & X & X & X & X & & & \\
 & X & X & X & X & X & & \\
 & & X & X & X & X & X & \\
 & & & X & X & X & X & X \\
 & & & X & X & X & X & X
\end{matrix}$$

- Eigenvectors of this matrix are solutions to the DE, with associated eigenvalue

Results

- Calculated the ground state of He and He*
- Off by some constant, independent of N or L
- Most accurate values (N=200k, L=150):
  - -25.21 eV (versus -24.59 eV)
  - -54.46 eV (versus -54.42 eV)





Future Work

- Try to fix the offset
- Implement more than two electrons
  - Breaks spherical symmetry, would require starting over
  - Probably not for this project
- H-F Method can be used for molecules, etc
  - Dangerously close to being a Chemist