Modeling strong-field ionization in small molecules

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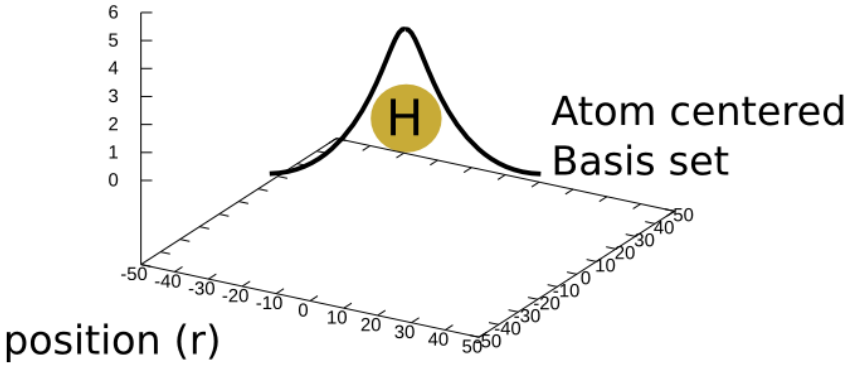
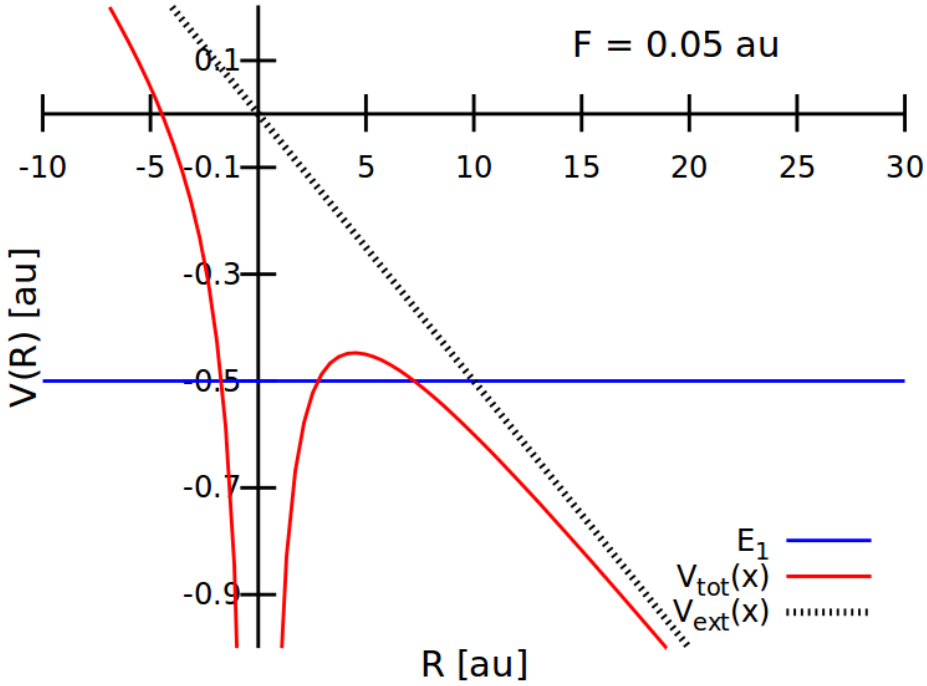
Recap

- Strong-field ionization
- Tunneling
- Basis sets





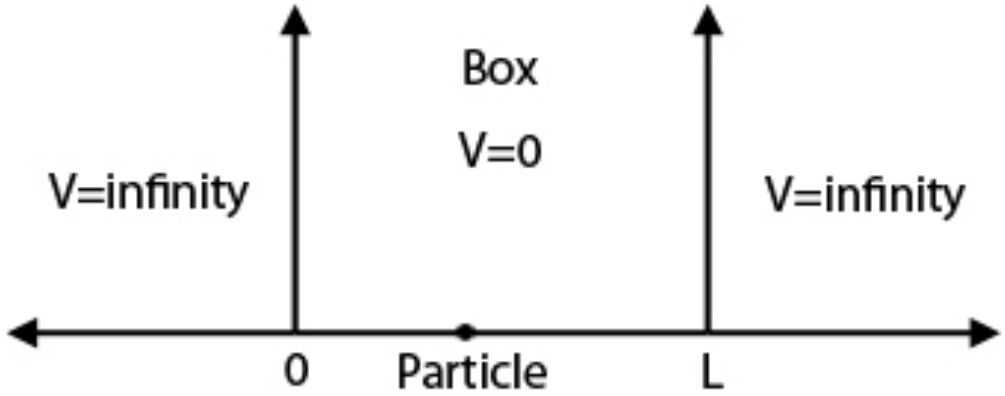
Goals

- learning the approximate wave functions to form a set
- engineering basis sets
- extending the density functional theory to strong-field
- find tunnel lengths in hydrogen atom

Achieved

- derived and understood wave functions for the particle in a box problem (PIB)
- created code to find energy levels of PIB with an electric field
- formed basis sets with wave functions
- studied polarizability of 1D “molecules”

Particle in a box



Particle in a box

- no potential acting on particle (free particle)
- Schrodinger Equation for free particle:

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\Psi(x) = 0$$

- Solution: $\Psi(x) = A\cos(kx) + B\sin(kx)$
- $\Psi(x)$ is probability a particle is in a region
- $\Psi(x)$ must be zero for barriers

Particle in a box

- $Bsin(ka)$ must be zero, so ka must be $n\pi$ for n= 1, 2, 3, ...
- Solving further reveals discrete energy levels

Code

- building phi
- symmetrical box
- new conditions

```
def phi(n, a, x):
    if (n%2 == 0): #even n
        val = math.sqrt(2.0/a)*math.sin(2.0*n*math.pi*x/a)
    else:          # odd n
        val = math.sqrt(2.0/a)*math.cos(n*math.pi*x/a)
    return val
```

Linear Combination of Wavefunction

- Basis set of wave functions constructs psi

$$\psi(x) = \sum_i c_i \phi_i(x)$$

- Optimize combination to minimize energy
- Best ground-state guess will be lowest eigenvalue from eigenvalue problem

Hamiltonian

- Eigenvalue problem

  $H\psi = E\psi$
- Hamiltonian operator:

  $H\psi = (H + V(x))\psi(x)$
- with electric field in box $V(x) = -Fqx$:

Code

- Construct matrix

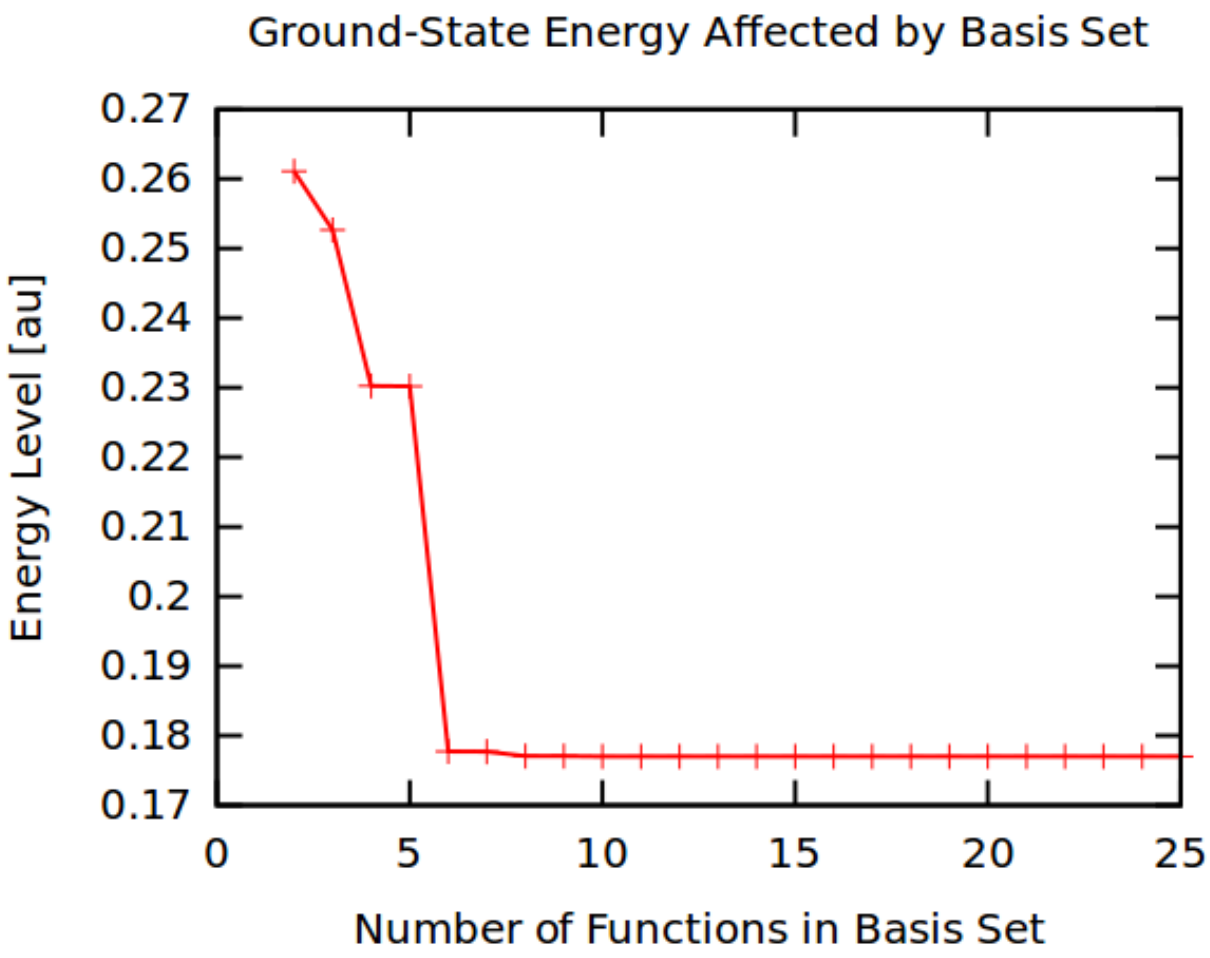
```
H_matrix= np.array( [ [ calc_Hnm(n, m) for m in range(1,10)] for n in range(1,10)] )
```

- Perform matrix operations. Pull lowest value

```
vals,vecs= LA.eigh(H_matrix)
idx = vals.argsort()
vals = vals[idx]
vecs= vecs[:,idx]
bestGuess= vals[0]
```

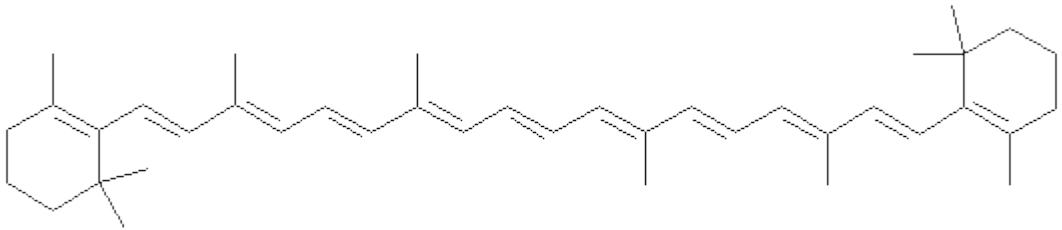
Basis Set

- A = 18.9 au
- F = .3 au



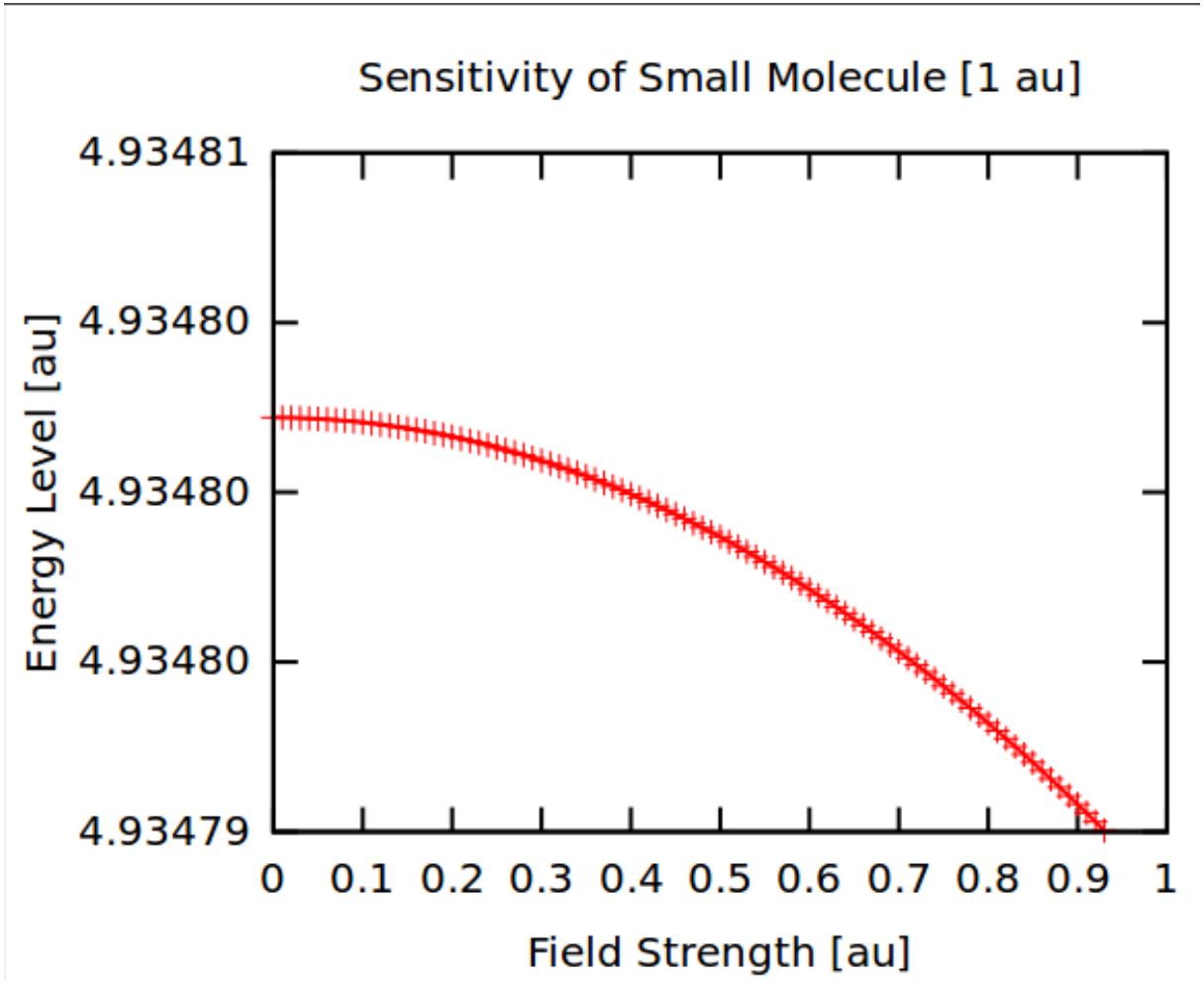
beta-Carotene

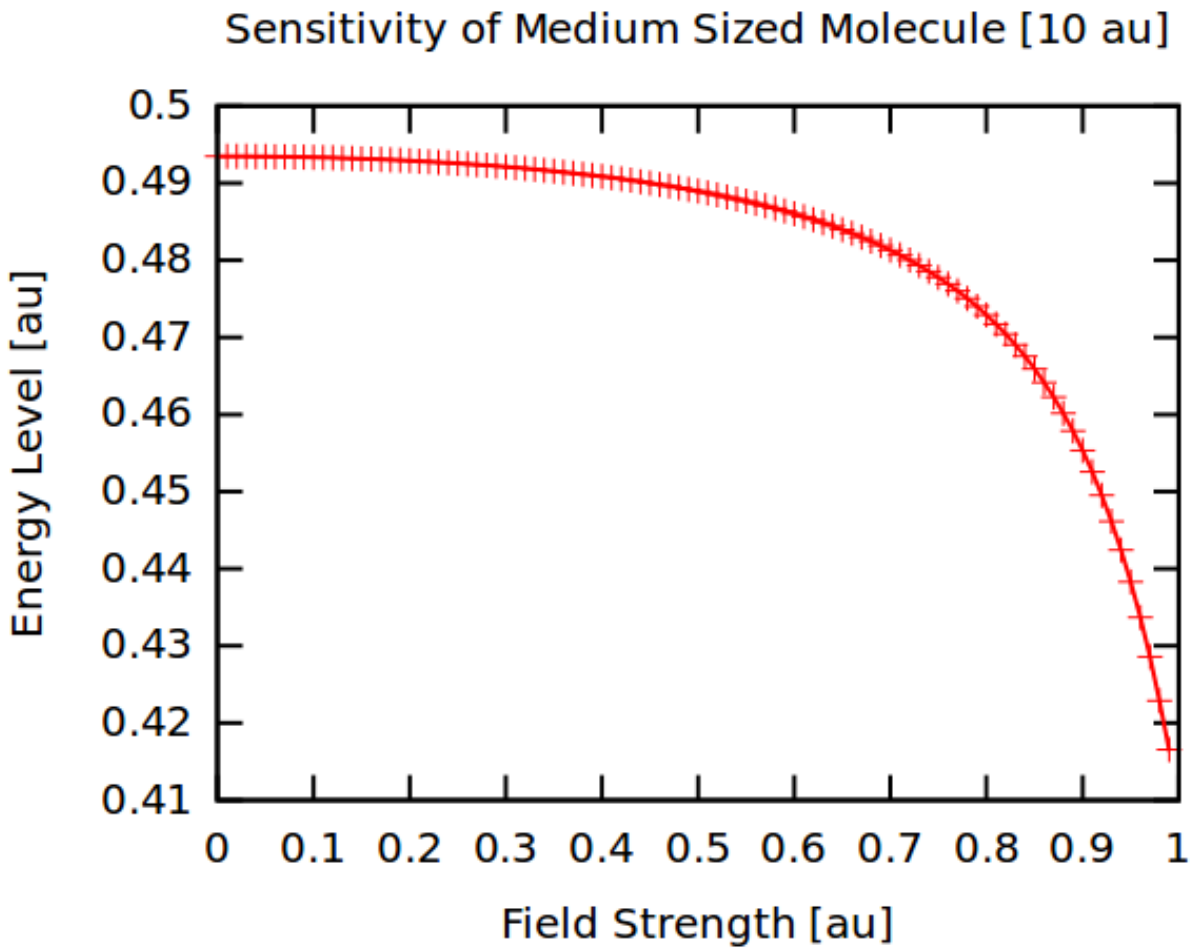
- bad model for molecules
- simple, linear ones do exist

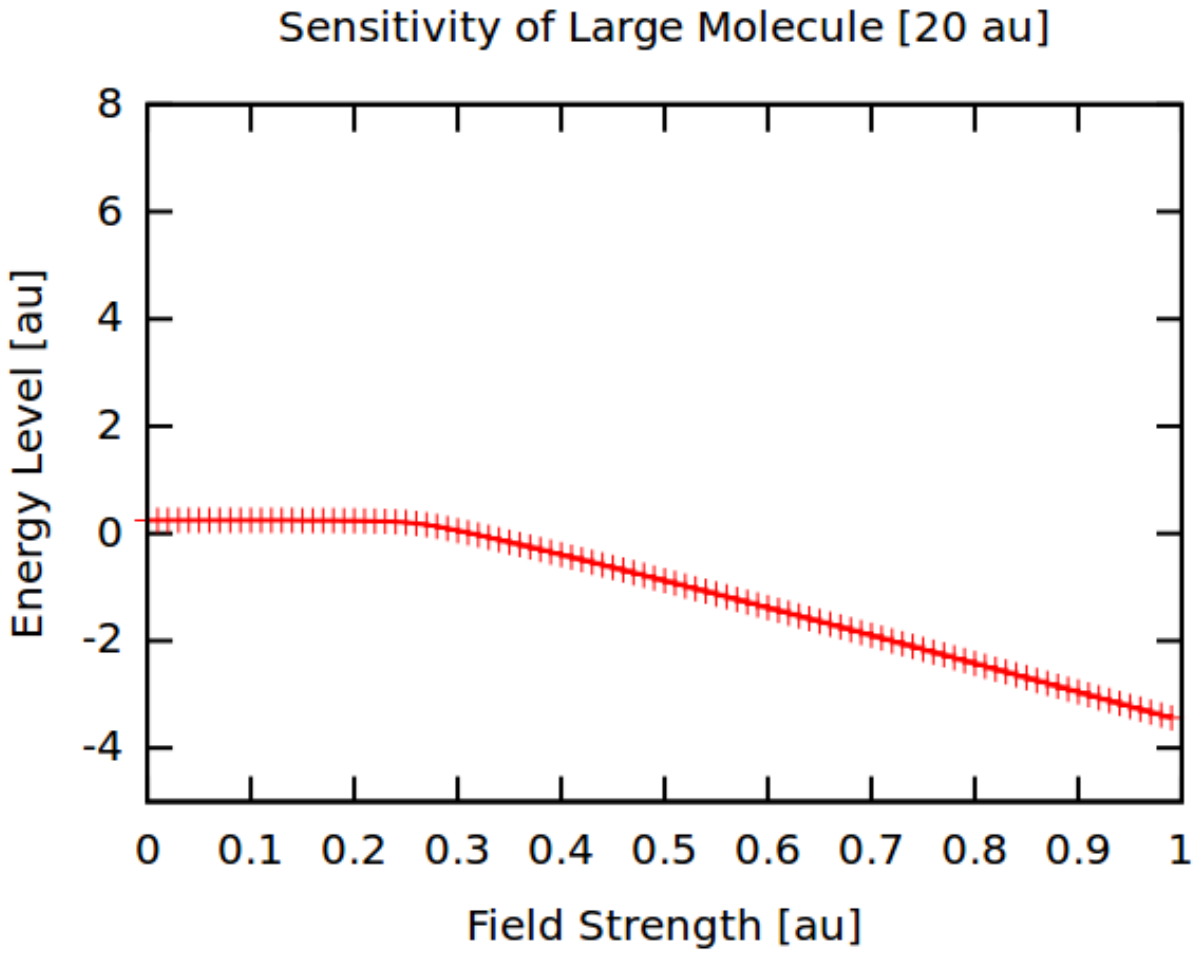


Length of molecules

- set basis at 25 functions
- set electric field at 0.3 au
- size of molecule will affect strength of field needed for ionization


Sensitivity of Small Molecule [1 au]
Energy Level [au]
4.93481
4.93480
4.93480
4.93480
4.93479
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Field Strength [au]


Sensitivity of Medium Sized Molecule [10 au]
Energy Level [au]
0.5
0.49
0.48
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Field Strength [au]


Sensitivity of Large Molecule [20 au]
Energy Level [au]
8
6
4
2
0
-2
-4
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Field Strength [au]

Polarizability

- inclination of a system to respond to an external force
- ground-state energy to be affected by field
- can provide insight to molecular structures

Location of Particle

- probability of location = ψ^2
- probability without an electric field

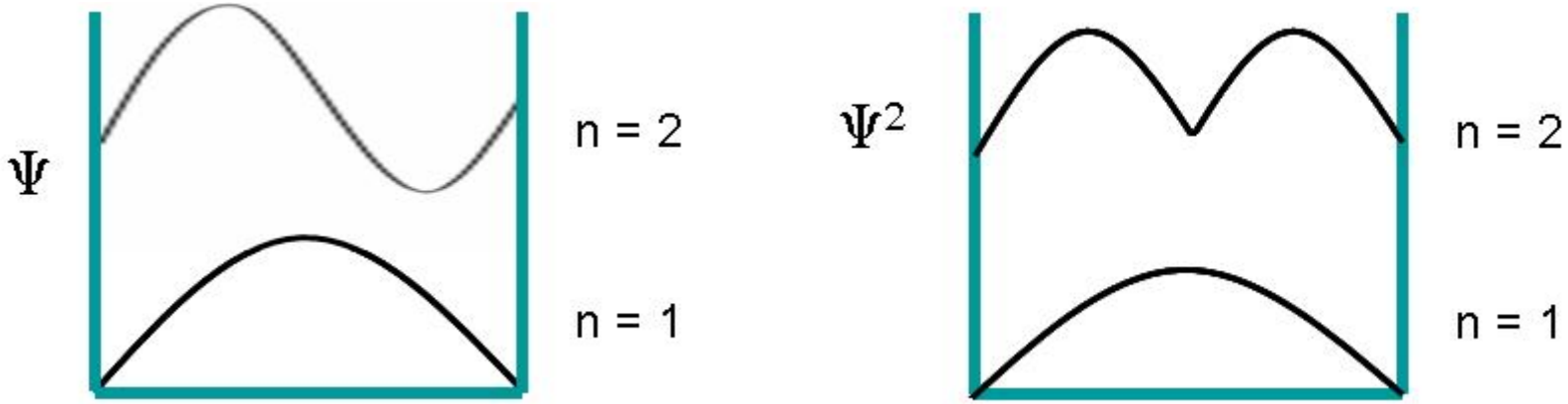
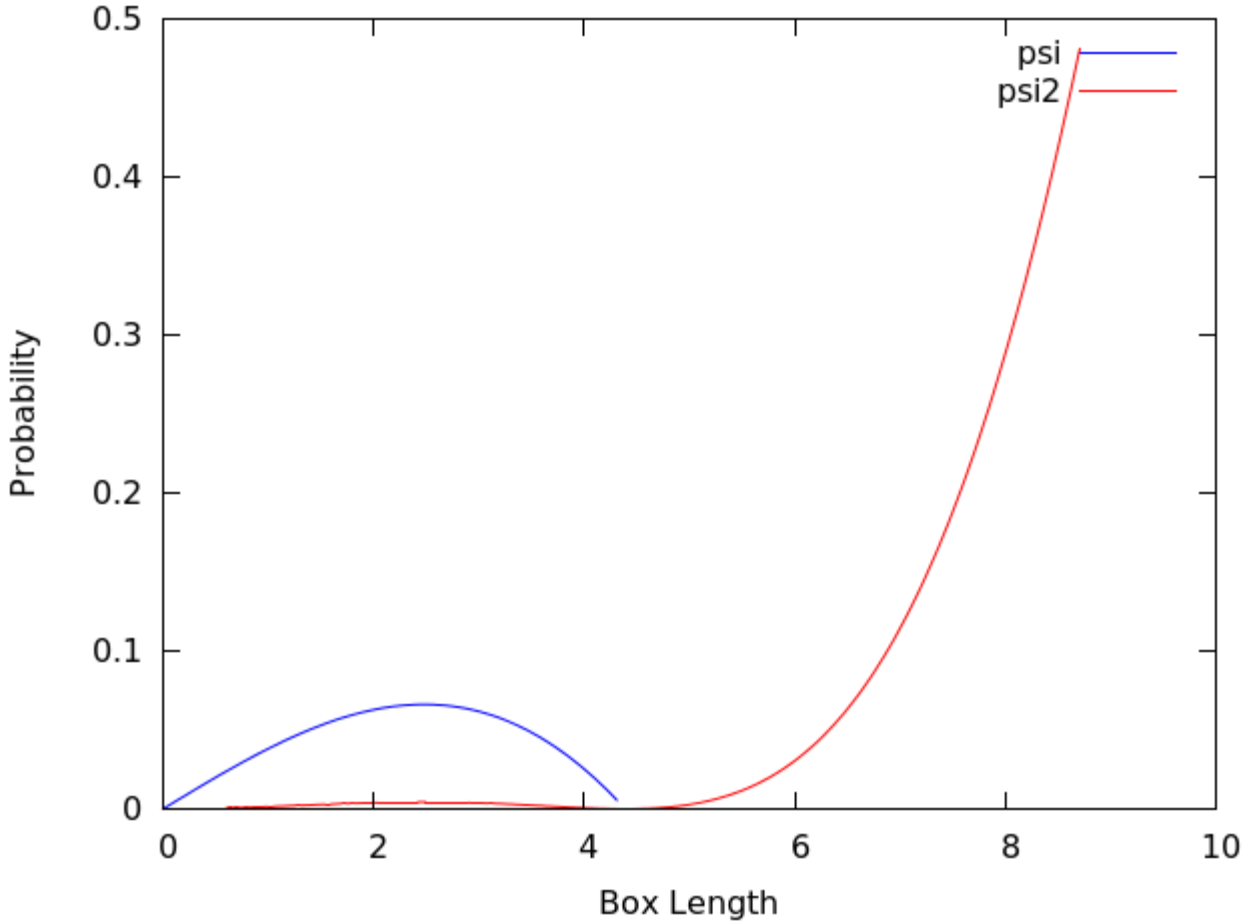


image source: http://chemwiki.ucdavis.edu

n= 1
F= .1 au



Future Work

- modify code for Hydrogen
- radial and angular parameters
- potentially expand for diatomic molecules
- add to code to find tunnel length

Acknowledgements

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