

Gradient geometry optimization leads us to a stationary point on PES
 $\text{grad}E=0$

It might be minimum, saddle point, inflection point, or maximum

How to find what the stationary point is (the nature of a stationary point)?

Like in calculus: get second derivatives of E on nuclear coordinates

$\frac{\partial^2 E}{\partial q_i^2} > 0$ All second derivatives are positive- minimum on PES

$\frac{\partial^2 E}{\partial q_i^2} = 0$ All second derivatives are positive but one equals to zero-inflection point on PES

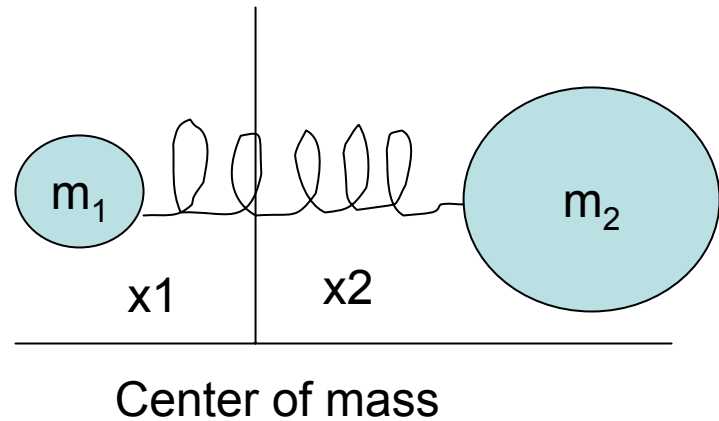
$\frac{\partial^2 E}{\partial q_i^2} < 0$ All second derivatives are positive but one is negative-saddle point on PES- TRANSITION STATE!

If we know second derivatives of E on q_i (the force constants) we can calculate some physical properties. The most important are harmonic vibrational frequencies- gives us ideal IR spectrum

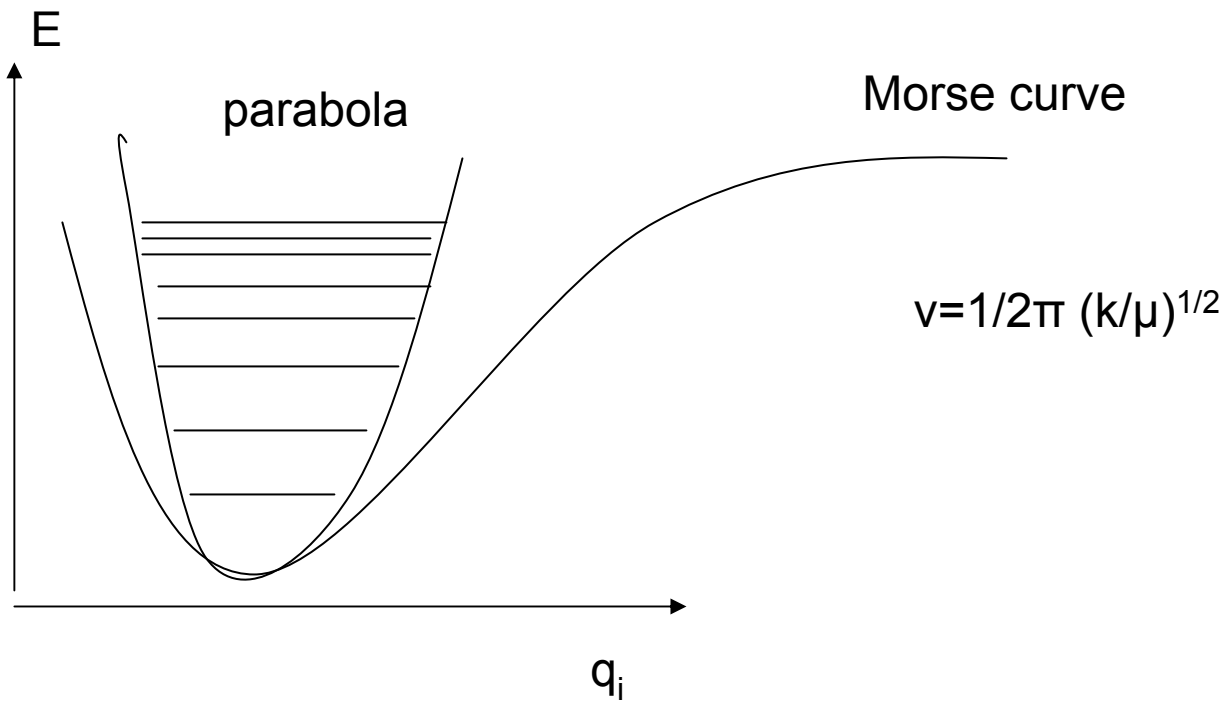
Classic harmonic oscillator

$F=-kx$, k is a spring force constant

$$\nu = 1/2\pi (k/\mu)^{1/2}$$



Use similar model for quantum harmonic oscillator



Use Born-Oppenheimer approximation: allow nuclei to vibrate with frozen wave function!

So, if we have one negative force, k ,
 The square root will give as $(-1)^{1/2} = i$, the
 imaginary unit. We'll get one imaginary
 frequency in the IR spectrum in G03
 denoted as “-”

Wave function. Molecular Orbitals as Linear Combination of Atomic Orbitals (MO LCAO)

Do we know exact AO for atoms?

Exact AO- tables of numbers

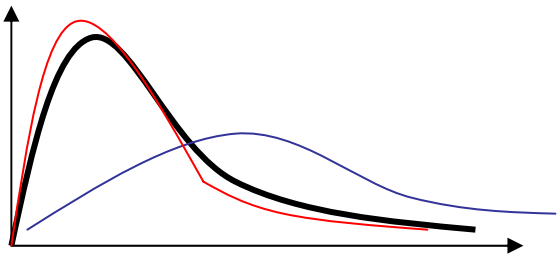
Approximate AO with a function

Approximate wave function with linear combination of exponential functions

Slater function

$$\varphi_{\text{AO}} = N(r^{n^*-1}e^{-\zeta_1 r} + r^{n^*-1}e^{-\zeta_2 r})$$

AO as a linear combination of two Slater functions with 2 zeta variables
Double-zeta basis set

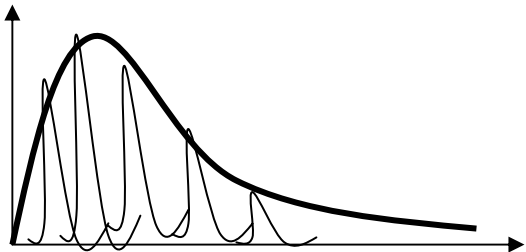


Black –true wave function
 Blue- one Slater function
 Red- Double-zeta

Two Slater functions provide good accuracy but integrals with e^{-r} are too complicated

Gauss functions (bell functions)

$$\varphi_{AO} = N_n(\alpha)r^{n-1} \exp(-\alpha r^2)$$



We shall need many Gauss functions to approximate wave function but integrals are easy to calculate, so overall it is faster

Basis Sets in G03

All-electron basis sets

Minimal basis set: STO-3G (Slater type orbital approximated with 3 G-functions)

Pople's basis sets

Split-valence basis sets

3-21G, 6-31G, 6-311G

We can add additional sets of G-functions: polarization (d,p,f) and diffuse (denoted as +)

6-31+G(d) 6-311++G(2df, p)

Effective core potential (ECP) basis sets. Core electrons are described with potential. Valence electrons- as above

For heavy atoms (starting from 4th period)

Relativistic core potential and associated basis sets

LanL2DZ (LanL-relativistic effective core potential, DZ-basis set for valence electrons) and SDD (Stuttgart –Dresden ECP and D-basis set)

Both model core electrons by a function
Treat valence electrons explicitly

Core can be taken from Dirac equation- relativistic calculations.
Simulate relativistic effects

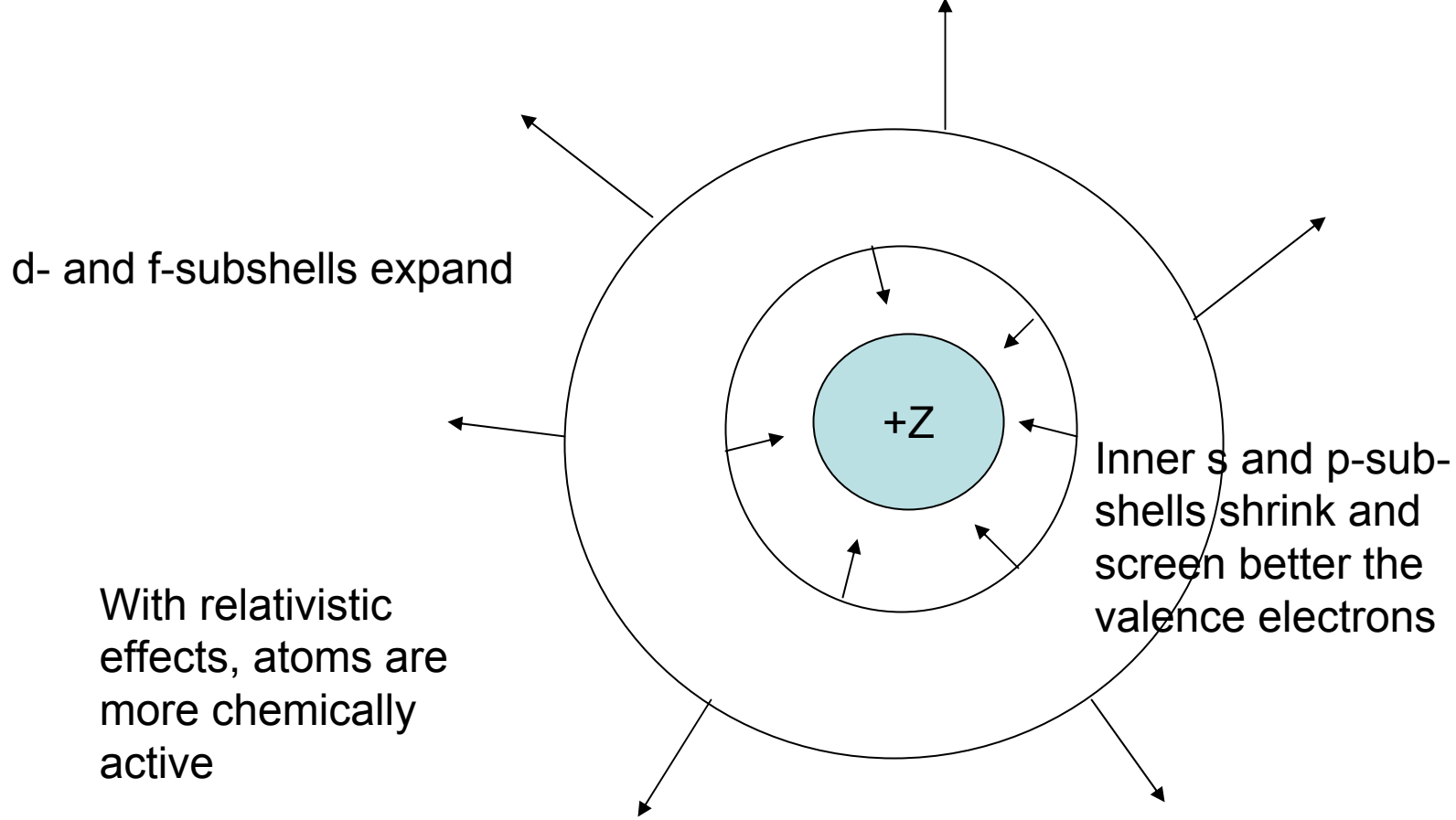
Relativistic effects (mass and velocity are related)

Special theory of relativity:
space-time symmetry

For H-like atom velocity of 1s electron is

$$v = Zc/137 \quad Z \text{ is a nuclear charge}$$

For heavy atoms, velocity of 1s e approaching speed of light- relativistic corrections are significant



So, LanL2DZ and SDD describe these sub-shell effects

Another result of relativistic effects- spin-orbit coupling. Big challenge!

In general, for any many-electron atom, inner subshells are less chemically important than valence electrons from outer shells

Go to contracted basis sets, contracted Gauss type orbital, CGTO

$$\text{CGTO} = \sum c_i \text{PGTO}$$

Primitive Gauss-type orbitals

Examples:

STO-3G

| | | | | | | |
|---|----|----|-----------------|-----------------|-----------------|---------------|
| C | 1s | 2s | 2p _x | 2p _y | 2p _z | 5CGTO, 15PGTO |
| H | 1s | | | | | 1CGTO, 3PGTO |

3-21G

| | | | | | | | | | |
|------|----|----|-----|-----------------|-------------------|-----------------|-------------------|-----------------|-------------------|
| C | 1s | 2s | 2s' | 2p _x | 2p _x ' | 2p _y | 2p _y ' | 2p _z | 2p _z ' |
| PGTO | 3 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 |

Overall, 15 PGTO and 9 CGTO

| | | | |
|------|----|-----|---------------|
| H | 1s | 1s' | 2CGTO, 4 PGTO |
| PGTO | 3 | 1 | |

$$6-31G(d) = 6-31G^*$$

C 1s 2s 2s' 2p_x2p_x' 2p_y2p_y' 2p_z 2p_z' d_{x²} d_{yz} dz² dxy dyz dzx
 6 3 1 3 1 3 1 3 1 1 1 1 1 1 1

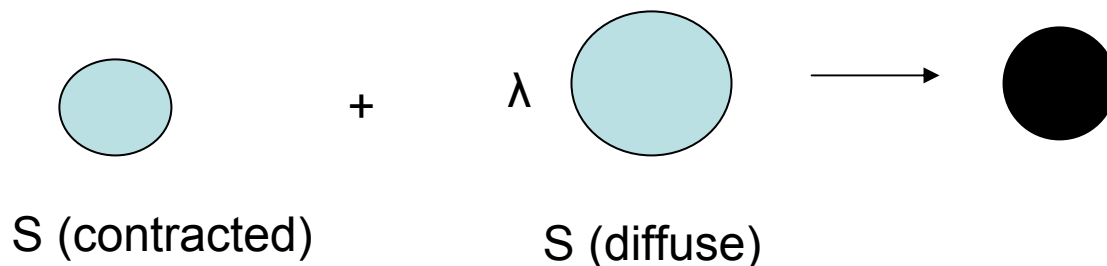
15 CGTO, 6+16+6=28 PGTO

H 1s 1s' 2CGTO, 4 PGTO
 3 1

Computational time is proportional to N^4 where N is number of basis functions

| C ₆ H ₆ | CGTO | PGTO |
|-------------------------------|------|------|
| STO-3G | 36 | 108 |
| 3-21G | 66 | 108 |
| 6-31G(d) | 102 | 192 |

Basis idea of diffuse and polarization functions



Diffuse functions are important whenever loosely bound electrons are present: Anions, excited states. Also for cations- to describe long-range interactions

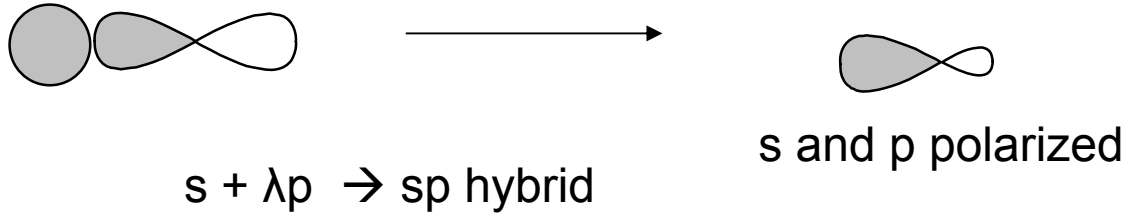
Polarization functions

A basis set that incorporates functions of higher angular quantum number (d for carbon, p for H) is called a polarization basis set.

It provides for displacement of electron density away from the nuclear center

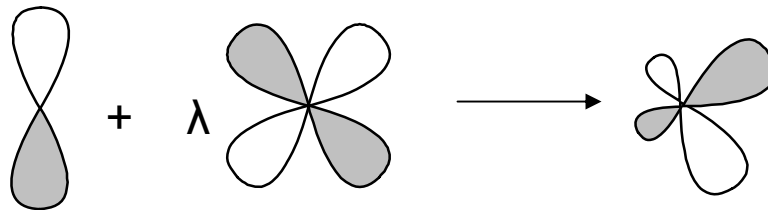
s polarized by p

How to describe polar H-F bond?



So, add polarization function to H (p for s-orbital)

p polarized by d



Now can describe nicely small bond angles

f-polarization functions allow to describe any volume of space around atom-expensive