Theoretical Chemistry

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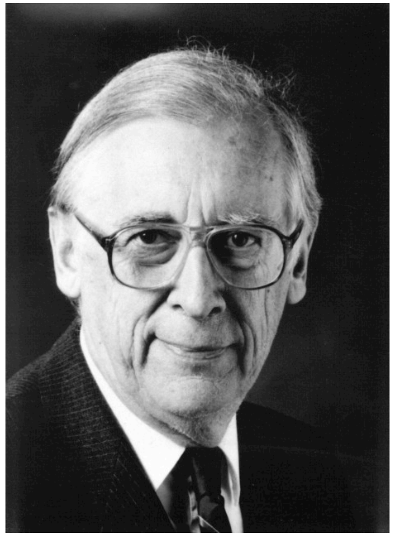
Summary

- The Hartree-Fock-Roothaan method
- **Pople and Dunning basis sets**
- Semiempirical models
- Configuration interaction
- Möller-Plesset perturbation theory
- Density functional theory
- Time-dependent DFT

Gaussian Basis Sets



John Pople
(1925-2004)

Split-valence Pople basis sets

General nomenclature

$$N - n_1 n_2 G$$

Core ← N $n_1 n_2$ → ***Valence***

Core orbitals are described by 1 contracted fonction (GTO)
This function is developed over N primitive Gaussian functions

$$AO(core) = GTO = \sum_{i=1}^{N} a_i \chi_i^G$$

Valence orbitals are described by 2 contracted fonctions (GTO_1 and GTO_2)
GTO_1 is developed over n_1 primitive Gaussian functions
GTO_2 is developed over n_2 primitive Gaussian functions

$$AO(valence) = c_1 GTO_1 + c_2 GTO_2 = c_1 \sum_{i=1}^{n1} a_i \chi_i^G + c_2 \sum_{i=1}^{n2} b_i \chi_i^{G'}$$

Example: 6-31G
1 contracted Gaussian function used per core orbital (combination of 6 primitives)
2 contracted Gaussian functions used per valence orbital (combination of 3 and 1 primitives, respectively)

GAUSSIAN BASIS SETS

Split-valence Pople basis sets

Adding polarization and diffuse functions

$$N - n_1 n_2 + G(x)$$

Diffuse ← +   (x) → ***polarization***

Polarization functions:

Enable to describe molecules with a charge flow between atoms having different electronegativities

Example: 6-31G(d)
d orbitals added on all non-hydrogen atoms
Example: 6-31G(d,p)
d orbitals added on all non-hydrogen atoms
p orbitals added on all hydrogen atoms

Diffuse functions:

Required for an accurate description of the outermost part of the electronic density and therefore to reproduce properties associated with the less bound electrons

Example: 6-31+G(d)
d orbitals added on all non-hydrogen atoms
sp orbitals added on all non-hydrogen atoms

GAUSSIAN BASIS SETS

Pople basis sets

Example: acetonitrile molecule CH_3CN

	core orbitals	*valence orbitals*
C	1s	2s, 2px, 2py, 2pz
C	1s	2s, 2px, 2py, 2pz
N	1s	2s, 2px, 2py, 2pz
H	/	1s
H	/	1s
H	/	1s
total	**3**	**15**

Double-zeta basis set

6-31G

1 contracted Gaussian function used per core orbital

2 contracted Gaussian functions used per valence orbital

N_{basis} = 3×1 + 15×2 = ***33 basis functions***

GAUSSIAN BASIS SETS

Pople basis sets

Example: acetonitrile molecule CH_3CN

	core orbitals	*valence orbitals*
C	1s	2s, 2px, 2py, 2pz
C	1s	2s, 2px, 2py, 2pz
N	1s	2s, 2px, 2py, 2pz
H	/	1s
H	/	1s
H	/	1s
total	**3**	**15**

Triple-zeta basis set

6-311G

1 contracted Gaussian function used per core orbital

3 contracted Gaussian functions used per valence orbital

N_{basis} = 3×1 + 15×3 = ***48 basis functions***

GAUSSIAN BASIS SETS

Pople basis sets

Example: acetonitrile molecule CH_3CN

	core orbitals	*valence orbitals*
C	1s	2s, 2px, 2py, 2pz
C	1s	2s, 2px, 2py, 2pz
N	1s	2s, 2px, 2py, 2pz
H	/	1s
H	/	1s
H	/	1s
total	**3**	**15**

Polarized triple-zeta basis set

6-311G(d) – also noted 6-311G*

1 contracted Gaussian function used per core orbital

3 contracted Gaussian functions used per valence orbital

5 *d* orbitals added on all non-hydrogen atoms

N_{basis} = 3×1 + 15×3 + 5x3 = ***63 basis functions***

GAUSSIAN BASIS SETS

Pople basis sets

Example: acetonitrile molecule CH_3CN

	core orbitals	*valence orbitals*
C	1s	2s, 2px, 2py, 2pz
C	1s	2s, 2px, 2py, 2pz
N	1s	2s, 2px, 2py, 2pz
H	/	1s
H	/	1s
H	/	1s
total	**3**	**15**

Polarized triple-zeta basis set

6-311G(d,p) – also noted 6-311G**

1 contracted Gaussian function used per core orbital

3 contracted Gaussian functions used per valence orbital

5 *d* orbitals added on all non-hydrogen atoms

3 *p* orbitals added on all hydrogen atoms

N_{basis} = 3×1 + 15×3 + 5x3 + 3x3 = ***72 basis functions***

Gaussian Basis Sets

Pople basis sets

Example: acetonitrile molecule CH_3CN

	core orbitals	*valence orbitals*
C	1s	2s, 2px, 2py, 2pz
C	1s	2s, 2px, 2py, 2pz
N	1s	2s, 2px, 2py, 2pz
H	/	1s
H	/	1s
H	/	1s
total	**3**	**15**

Polarized triple-zeta basis set with diffuses

6-311+G(d,p) – also noted 6-311+G**

1 contracted Gaussian function used per core orbital

3 contracted Gaussian functions used per valence orbital

5 *d* orbitals added on all non-hydrogen atoms

3 *p* orbitals added on all hydrogen atoms

3 *sp* orbitals added on all non-hydrogen atoms

N_{basis} = 3×1 + 15×3 + 5x3 + 3x3 + 3x3 = ***81 basis functions***

GAUSSIAN BASIS SETS

‘correlation-consistent’ polarized Dunning basis sets

General nomenclature

$$\mathrm{cc}-\mathrm{p}\underbrace{\mathrm{VXZ}}$$

‘correlation consistent’ (CISD)

Valence X-zeta

Polarization functions *already included*

Example: cc-pVDZ
Double-zeta valence polarized basis set
cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z

Diffuse functions can also be added

Example: aug-cc-pVDZ
Augmented cc-pVDZ basis set: 1 set of diffuse functions is added

Example: d-aug-cc-pVDZ
Double augmented cc-pVDZ basis set: 2 sets of diffuse functions are added

Thom Dunning

GAUSSIAN BASIS SETS

‘correlation-consistent’ polarized Dunning basis sets

Example: acetonitrile molecule CH_3CN

cc-pVDZ

	core orbitals	*valence orbitals*	*valence expansion*	*polarisation orbitals*	*diffuse orbitals*	*Total*
C_1	1	4 [s, p]	2 (*double-ζ*)	5 [d]	0	14=1+4x2+5
C_2	1	4 [s, p]	2 (*double-ζ*)	5 [d]	0	14=1+4x2+5
N	1	4 [s, p]	2 (*double-ζ*)	5 [d]	0	14=1+4x2+5
H_1	0	1 [s]	2 (*double-ζ*)	3 [p]	0	5=0+1x2+3
H_2	0	1 [s]	2 (*double-ζ*)	3 [p]	0	5=0+1x2+3
H_3	0	1 [s]	2 (*double-ζ*)	3 [p]	0	5=0+1x2+3
total	**3**	**15**	**2**	**24**	**0**	**57=3+15x2+24**

cc-pVDZ = split-valence double-ζ core, plus single polarization function
similar to 6-31G**

GAUSSIAN BASIS SETS

‘correlation-consistent’ polarized Dunning basis sets

Example: acetonitrile molecule CH_3CN

cc-pVTZ

	core orbitals	*valence orbitals*	*valence expansion*	*polarisation orbitals*	*diffuse orbitals*	*Total*
C_1	1	4 [s, p]	3 (*triple-ζ*)	17 [d, d, f]	0	30=1+4x3+17
C_2	1	4 [s, p]	3 (*triple-ζ*)	17 [d, d, f]	0	30=1+4x3+17
N	1	4 [s, p]	3 (*triple-ζ*)	17 [d, d, f]	0	30=1+4x3+17
H_1	0	1 [s]	3 (*triple-ζ*)	11 [p, p, d]	0	14=0+1x3+11
H_2	0	1 [s]	3 (*triple-ζ*)	11 [p, p, d]	0	14=0+1x3+11
H_3	0	1 [s]	3 (*triple-ζ*)	11 [p, p, d]	0	14=0+1x3+11
total	**3**	**15**	**3**	**84**	**0**	**132=3+15x3+84**

cc-pVTZ = split-valence triple-ζ core, plus two *d* and one *f* function on first row atoms, and two *p* and one *d* functions on hydrogens.
Similar to 6-311G(2d1f,2p1d)

GAUSSIAN BASIS SETS

‘correlation-consistent’ polarized Dunning basis sets

Example: acetonitrile molecule CH_3CN

aug-cc-pVDZ

	core orbitals	*valence orbitals*	*valence expansion*	*polarisation orbitals*	*diffuse orbitals*	*Total*
C_1	1	4 [s, p]	2 (*double-ζ*)	5 [d]	9 [s, p, d]	23=1+4x2+5+9
C_2	1	4 [s, p]	2 (*double-ζ*)	5 [d]	9 [s, p, d]	23=1+4x2+5+9
N	1	4 [s, p]	2 (*double-ζ*)	5 [d]	9 [s, p, d]	23=1+4x2+5+9
H_1	0	1 [s]	2 (*double-ζ*)	3 [p]	4 [s, p]	9=0+1x2+3+4
H_2	0	1 [s]	2 (*double-ζ*)	3 [p]	4 [s, p]	9=0+1x2+3+4
H_3	0	1 [s]	2 (*double-ζ*)	3 [p]	4 [s, p]	9=0+1x2+3+4
total	**3**	**15**	**2**	**24**	**39**	**96=3+15x2+24+39**

aug-cc-pVDZ = same as cc-pVDZ plus one diffuse function per each angular momentum present in cc-pVDZ.

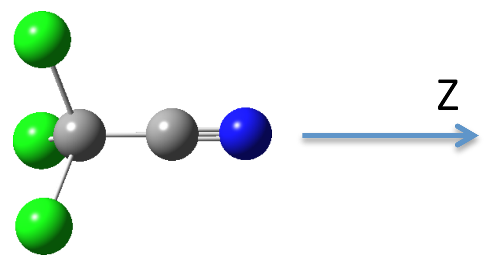
EXAMPLE CALCULATIONS WITH DUNNING BASIS SETS

Molecular dipole and polarizabilities

responses of the dipole moment to an external electric field F

$$\mu = \mu_0 + \alpha F + \beta F^2 + \ldots$$

μ_0 = permanent dipole moment
α = linear polarizability
β = first (nonlinear) hyperpolarizability



Example: acetonitrile molecule CH_3CN

Absolute values (atomic units)

	μ_z	α_{zz}	β_{zzz}
DZ	1,67556	38,03976	11,68561
TZ	1,67364	38,09252	13,47772
QZ	1,67295	38,07922	13,96194
5Z	1,67273	38,07417	13,90807
6Z	1,67273	38,07515	13,89610

Relative errors (%)

	μ_z	α_{zz}	β_{zzz}
DZ	-0,1690	0,0929	15,9073
TZ	-0,0543	-0,0456	3,0108
QZ	-0,0131	-0,0107	-0,4738
5Z	-0,0003	0,0026	-0,0861
6Z	0,0000	0,0000	0,0000

Example Calculations with Dunning Basis Sets

Molecular dipole and polarizabilities

responses of the dipole moment to an external electric field F

$\mu = \mu_0 + \alpha F + \beta F^2 + \ldots$

μ_0 = permanent dipole moment
α = linear polarizability
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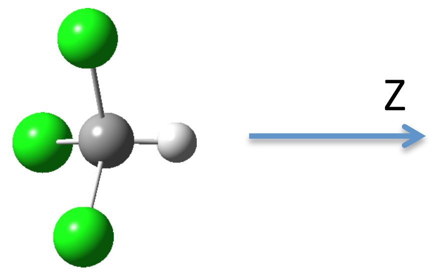


Example: chloroform molecule $CHCl_3$

Absolute values (atomic units)

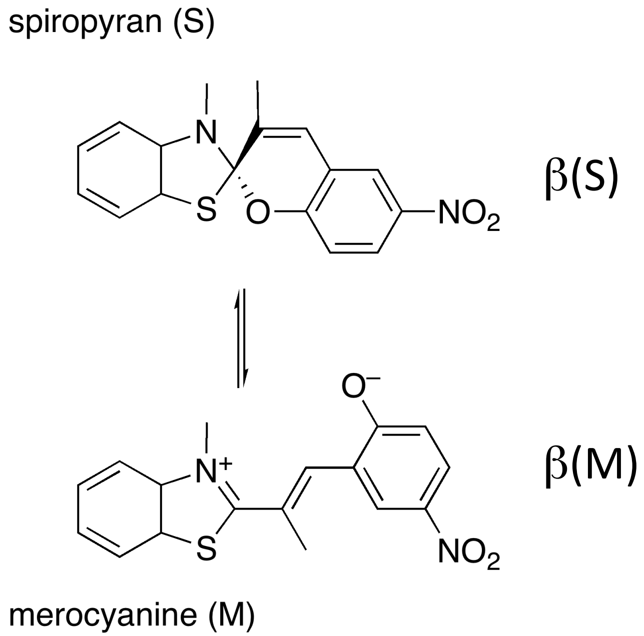
	μ_z	α_{zz}	β_{zzz}
DZ	0.481	41.256	2.403
TZ	0.478	42.823	9.222
QZ	0.475	43.195	13.549
6Z	0.472	43.292	13.559

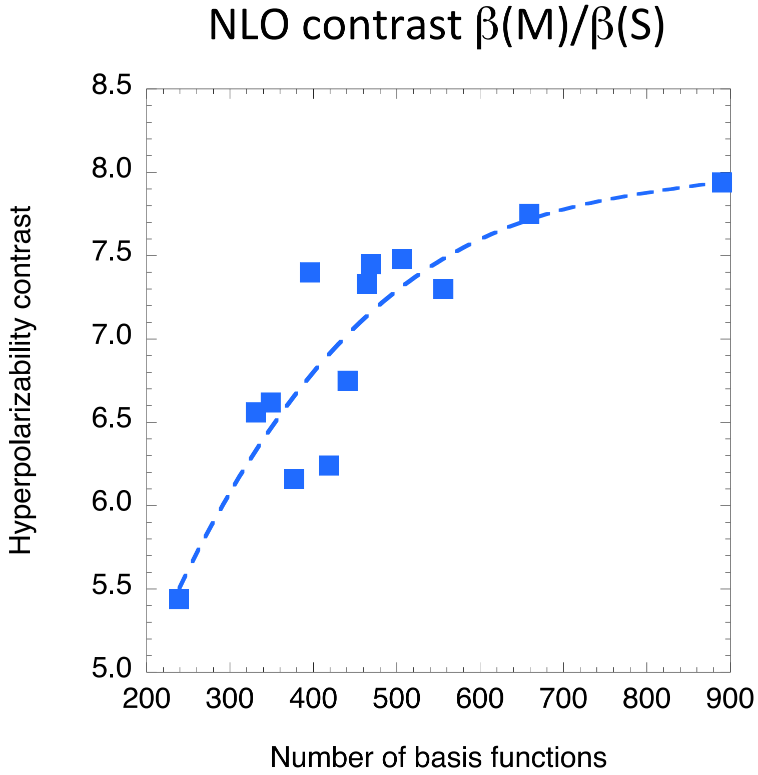
Relative errors (%)

	μ_z	α_{zz}	β_{zzz}
DZ	-1.825	4.703	82.275
TZ	-1.259	1.082	31.984
QZ	-0.573	0.223	0.074
6Z	0.000	0.000	0.000

Example Calculations: Nonlinear Optical Switches

Basis set effect on nonlinear optical contrasts





A. Plaquet et al. *Phys. Chem. Chem. Phys.* **2008**, 10, 6223

GAUSSIAN BASIS SETS

Conclusions

Basis set
core (minimal/double-ζ/triple-ζ) [+ polarization functions [+ diffuse functions]]

Polarization functions
should always be used for, at least, heavy atoms (first-row and beyond).

Diffuse functions
should be used for computations on systems involving anions and/or non-bonding interactions.

Special basis sets for correlated calculations
(Dunning correlation-consistent basis sets…).

http://www.emsl.pnl.gov/forms/basisform.html - EMSL Gaussian Basis Set database

BASIS SET EXCHANGE