

Configuration Interaction

The Full CI wavefunction

$$|\Psi_{FCI}\rangle = \sum_i c_i |\Phi_i\rangle$$

Contains all possible Slater Determinants (SD), or more generally Configuration State Functions (CSF) with a given spin and symmetry that can be generated for a certain basis set.

It is often written with reference to the Hartree-Fock wavefunction

$$|\Psi_{FCI}\rangle = a_0 |\Phi_0\rangle + \sum_{i,a} a_i^a |\Phi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} a_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} a_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots$$

Or simply

$$|\Psi_{FCI}\rangle = a_0 |\Phi_0\rangle + \sum_S a_S |\Phi_S\rangle + \sum_D a_D |\Phi_D\rangle + \sum_T a_T |\Phi_T\rangle + \dots$$

Slater Determinants and Configuration State Functions

$$\Phi(\mathbf{t}_1 \dots \mathbf{t}_N) = \hat{A}[\mathbf{y}_1(\mathbf{t}_1) \dots \mathbf{y}_N(\mathbf{t}_N)] \quad \hat{A} - \text{antisymmetrization operator}$$

$$\hat{A}[\mathbf{y}_1(\mathbf{t}_1) \dots \mathbf{y}_N(\mathbf{t}_N)] = \frac{1}{N!} \sum_P e_P \mathbf{y}_1(\mathbf{t}_{P(1)}) \dots \mathbf{y}_N(\mathbf{t}_{P(N)}) \quad e_P \text{ is the sign of the permutation } P$$

$$\Phi(\mathbf{t}_1 \dots \mathbf{t}_N) = \frac{1}{N!} \begin{vmatrix} \mathbf{y}_1(\mathbf{t}_1) & \dots & \mathbf{y}_1(\mathbf{t}_N) \\ \vdots & \vdots & \vdots \\ \mathbf{y}_N(\mathbf{t}_1) & \dots & \mathbf{y}_N(\mathbf{t}_N) \end{vmatrix}$$

SDs are not necessarily pure eigenstates of \hat{S}^2 but will also mix in other values of s . This is rectified by the use of CSFs, through the use of the spin-projection operator \hat{O}_s

$$\hat{O}_s = \prod_{k \neq s} \frac{\hat{S}^2 - \hbar^2 k(k+1)}{\hbar^2 s(s+1) - \hbar^2 k(k+1)} \quad \text{where } k = N/2, (N/2)-1, \dots, 0 \text{ or } 1/2 \text{ except for } k = s.$$

The Hartree-Fock approximation

The HF wavefunction is a N electron wavefunction Φ constructed from N one-electron spin-orbitals $\mathbf{y}_i(\mathbf{t})$ in an antisymmetric fashion

$$\Phi(\mathbf{t}_1 \dots \mathbf{t}_N) = \frac{1}{N!} \begin{vmatrix} \mathbf{y}_1(\mathbf{t}_1) & \dots & \mathbf{y}_1(\mathbf{t}_N) \\ \vdots & \vdots & \vdots \\ \mathbf{y}_N(\mathbf{t}_1) & \dots & \mathbf{y}_N(\mathbf{t}_N) \end{vmatrix}$$

A closed shell HF state is represented by a variationally optimized Slater determinant. Such a wavefunction represents a state where each electron behaves as an independent particle (subject to Fermi correlation). This state is determined by solving an effective one-electron Schrödinger equation which generates one independent-particle solution (spin orbital) for each electron in the system. The final N electron state is then obtained as an antisymmetrized product of N independent eigenfunctions of the effective Hamiltonian of the one electron Schrödinger equation.

The Hartree-Fock equation

HF builds on the fact that the Schrödinger equation can be solved for one electron systems, like hydrogen.

$$\hat{F}\mathbf{y}_i(t) = e_i\mathbf{y}_i(t)$$

where \hat{F} is the Fock operator and e_i is the orbital energy. The spin orbitals are eigenfunctions of the Fock operator.

$$\hat{F}|\Phi_0\rangle = \sum_I^{occ} e_I |\Phi_0\rangle$$

It is important to realize that, although the HF wavefunction is an eigenfunction to the Fock operator with an eigenvalue equal to the sum of the orbital energies, this eigenvalue is not the same as the HF energy. The HF energy is the expectation value of the true Hamiltonian.

Basis sets

In addition to using an effective one electron Schrödinger equation, the wavefunction (spin orbitals) are created from linear combinations of atom centered basis functions. This set of basis functions makes out the space that the electrons can occupy, and is called the basis set.

Basis sets have been created for the atoms in the periodic table through atomic calculations. E.g. for carbon there will be 1s, 2s and 2p basis functions with exponents (and contraction coefficients) determined from carbon atom calculations, which are used in molecular calculations where only the amount of contribution of the individual basis functions is optimized. In a strict sense, the size (exponent), the position (fixed to be atom centered) and the contribution should be optimized in molecular calculations, because this would be ‘non-linear’ optimizations. The size of the basis functions is compensated by using linear combinations of different

sizes to form one ‘atomic orbital’ AO, and the fixed position of the basis functions is compensated by adding polarization functions – basis functions of higher angular momentum quantum numbers. For carbon; d and f ... functions.

Suitable, flexible basis sets with different accuracies have been constructed in order to only have to do linear optimizations in the calculations.

- Split valence – 1 basis function per core AO and 2, 3, ... basis functions to describe the valence AOs.
- Addition of diffuse basis functions to extend the space for the electrons for the description of anions, excited states, polarizability, etc.

MO-LCAO

Atomic Orbitals – usually not explicitly constructed, but basis functions serves the same purpose.

basis functions - linear combination (contraction) of primitives

primitives – gaussian functions

Symmetry Orbitals – linear combinations of basis functions (also a sort of contraction)

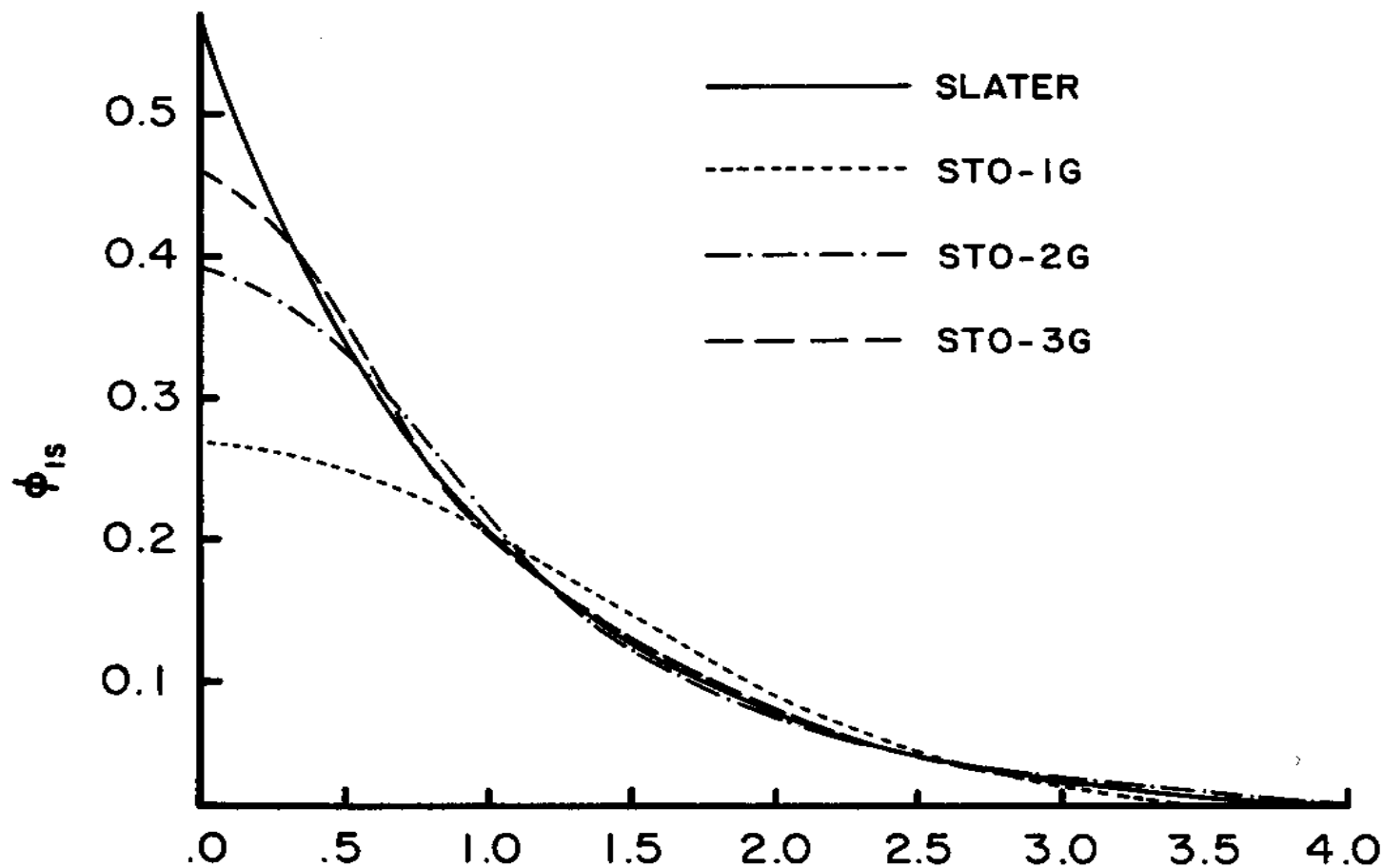
Transformation from AO to MO integrals

$$\langle i | \hat{h} | j \rangle = \sum_m \sum_n h_{mn} c_{mi} c_{nj} \quad 1 \text{ electron integrals}$$

$$\langle ij | kl \rangle = \sum_m \sum_n \sum_l \sum_s \langle \mathbf{mn} | \mathbf{ls} \rangle c_{mi} c_{nj} c_{lk} c_{sl} \quad 2 \text{ electron integrals}$$

Slater functions vs. Gaussian functions

Slater functions are more like hydrogen type functions.



The total number of SDs

$$\binom{N}{n} \binom{M-N}{n}$$

n electrons
M spin orbitals
N occupied spin orbitals

Not all SDs will contribute to the wavefunction - only SDs with the correct spin and space symmetry.

Linear combinations of SDs that are eigenfunctions of \hat{S}^2 are used
– Configuration State Functions

Still a very large problem to solve

Common approximations to FCI

Full CI in restricted space

- Only treat valence electrons
- Only include a selection of valence electrons – active electrons
- Discard virtual orbitals that are very high in energy – active space

CAS-CI, Complete Active Space – CI

Truncation of the CI wavefunction expansion

Only include excitations up to a certain level

CISD, CISDT, CISDTQ

$$|\Psi_{CISD}\rangle = a_0|\Phi_0\rangle + \sum_S a_S|\Phi_S\rangle + \sum_D a_D|\Phi_D\rangle$$

CISD is still a large problem – grows fast with the size of the system

CI calculations on H₂O

Truncation	RHF	CISD	CISDT	CISDTQ	CISDTQP
E-E _{FCI}	0.21782	0.012024	0.009043	0.000327	0.000139

At CISDT the energy is 94.5% of FCI

The reference configuration - Usually the HF wavefunction

What about cases where HF is not a good solution for the system?

Strong reference, single determinant dominant cases are less complicated.

Multi reference CI:

1. MCSCF – Multi Configuration SCF ~ very small CI expansion with just a few determinants.
2. Do truncated CI for all these determinants

$$\begin{aligned} |\Psi_{MRCISD}\rangle = & a_0|\Phi_0\rangle + \sum_{S_0} a_{S_0}|\Phi_{S_0}\rangle + \sum_{D_0} a_{D_0}|\Phi_{D_0}\rangle \\ & + a_1|\Phi_1\rangle + \sum_{S_1} a_{S_1}|\Phi_{S_1}\rangle + \sum_{D_1} a_{D_1}|\Phi_{D_1}\rangle \\ & + a_2|\Phi_2\rangle + \sum_{S_2} a_{S_2}|\Phi_{S_2}\rangle + \sum_{D_2} a_{D_2}|\Phi_{D_2}\rangle \\ & \vdots \end{aligned}$$

The CI Schrödinger equation

$$\hat{H}|\Psi_{CI}\rangle = E_{CI}|\Psi_{CI}\rangle$$

$$E_{CI} = \min_{a_I} \frac{\langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle}{\langle \Psi_{CI} | \Psi_{CI} \rangle}$$

The minimization involves the determination of the parameters a_I that gives the lowest energy through a_I , variational parameters.

The derivatives of the CI wavefunction with respect to the variational parameters are particularly simple:

$$\frac{\partial}{\partial a_I} |\Psi_{CI}\rangle = |\Phi_I\rangle$$

This leads to the standard eigenvalue problem of the CI coefficients - a projected Schrödinger equation:

$$\langle \Phi_I | \hat{H} | \Psi_{CI} \rangle = E_{CI} \langle \Phi_I | \Psi_{CI} \rangle$$

The principle steps to solve the CI equation are:

1. Calculate the H matrix $H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$
2. Diagonalize H – find the lowest eigenvalue

FCI variational and size consistent

- Variational – approaches the correct energy from above. Built in to the CI Schrödinger equation. All (most) truncated CI are variational.
- Size extensivity – size consistency. A method (energy) should scale correctly with the number of electrons.
- Consequence: The energy of a super system made up of two non interacting molecules (100 Å apart) should give twice the energy of a calculation of only one of the molecules.
 - Only fulfilled by FCI
 - Can be corrected for in truncated CI (e.g QCISDT)
 - MP, MBPT, and CC methods are size extensive (but not variational)

Matrix elements H_{IJ} are calculated using Slater rules $H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle$

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h} | j \rangle + \frac{1}{2} \sum_{i \neq j} \sum [\langle ij | ij \rangle - \langle ij | ji \rangle]$$

$$\sum_i \langle i | \hat{h} | j \rangle + \frac{1}{2} \sum_{i \neq j} \sum \langle ij || ij \rangle = E_{HF}$$

Where \hat{h} is the Fock operator.

$$\langle ij || ij \rangle = \iint \mathbf{y}_i^*(1) \mathbf{y}_j^*(2) \frac{1}{r_{ij}} (1 - \hat{P}_{12}) \mathbf{y}_i(1) \mathbf{y}_j(2) dt_1 dt_2 \quad \hat{P}_{12} \text{ permutes electron 1 and 2}$$

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = 0$$

$$\langle \Phi_i^a | \hat{H} | \Phi_j^a \rangle = \langle i | \hat{h} | j \rangle + \frac{1}{2} \sum_{k \neq i, j} \langle ik || jk \rangle$$

$$\langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle = \langle ij || ab \rangle$$

$$\langle \Phi_0 | \hat{H} | \Phi_{ijk}^{abc} \rangle = \langle \Phi_0 | \hat{H} | \Phi_{ijkl}^{abcd} \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ij}^{cd} \rangle = \langle ab || cd \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{kl}^{ab} \rangle = \langle kl || ij \rangle$$

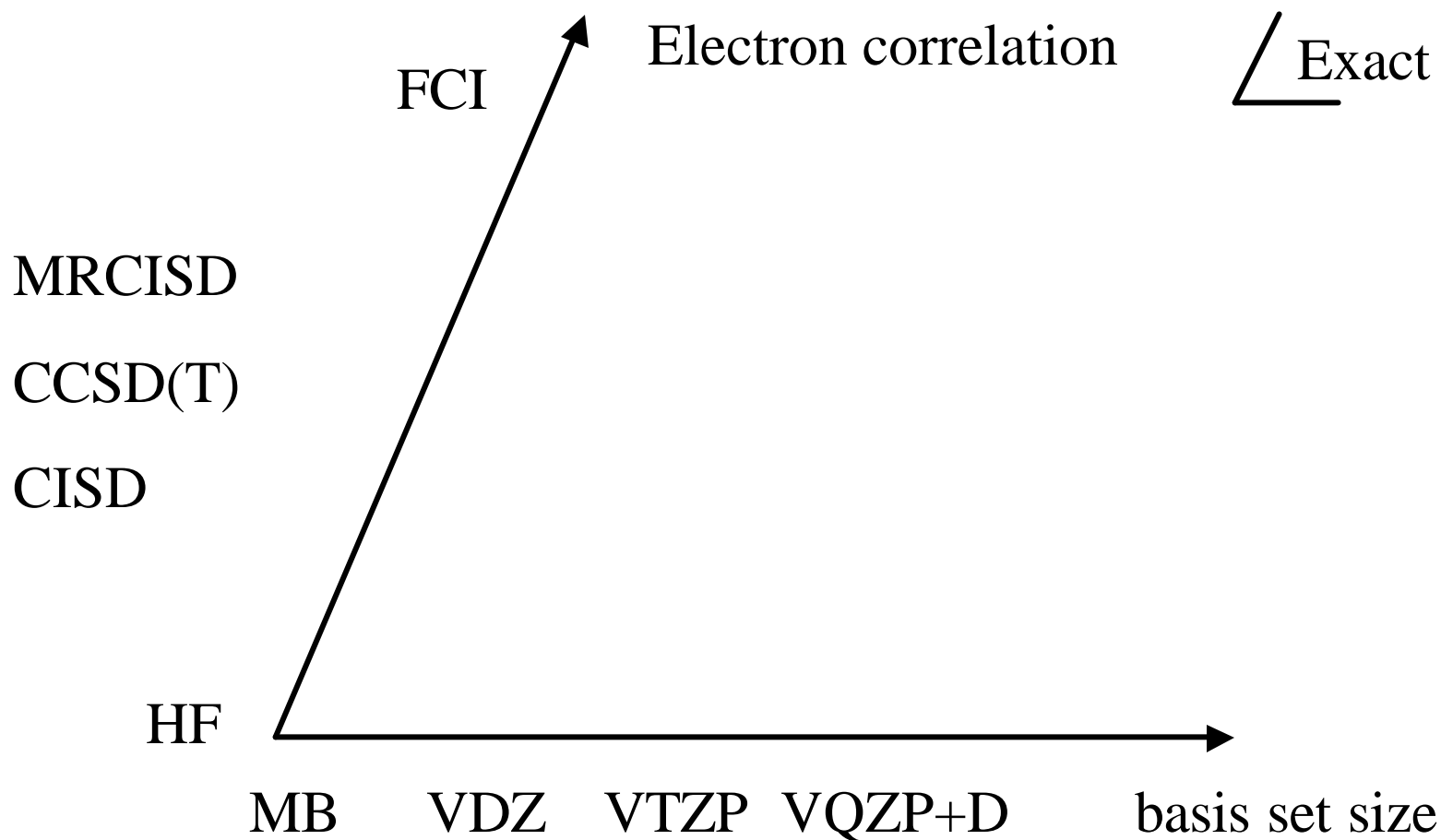
Conceptual structuring of the H matrix

	$ \Phi_0\rangle$	$ S\rangle$	$ D\rangle$	$ T\rangle$	$ Q\rangle$
$\langle\Phi_0 $	E_{HF}	0	$\langle\Phi_0 \hat{H} D\rangle$	0	0
$\langle S $.	$\langle S \hat{H} S\rangle$	$\langle S \hat{H} D\rangle$	$\langle S \hat{H} T\rangle$	0
$\langle D $.	.	$\langle D \hat{H} D\rangle$	$\langle D \hat{H} T\rangle$	$\langle D \hat{H} Q\rangle$
$\langle T $.	.	.	$\langle T \hat{H} T\rangle$	$\langle T \hat{H} Q\rangle$
$\langle Q $	$\langle Q \hat{H} Q\rangle$

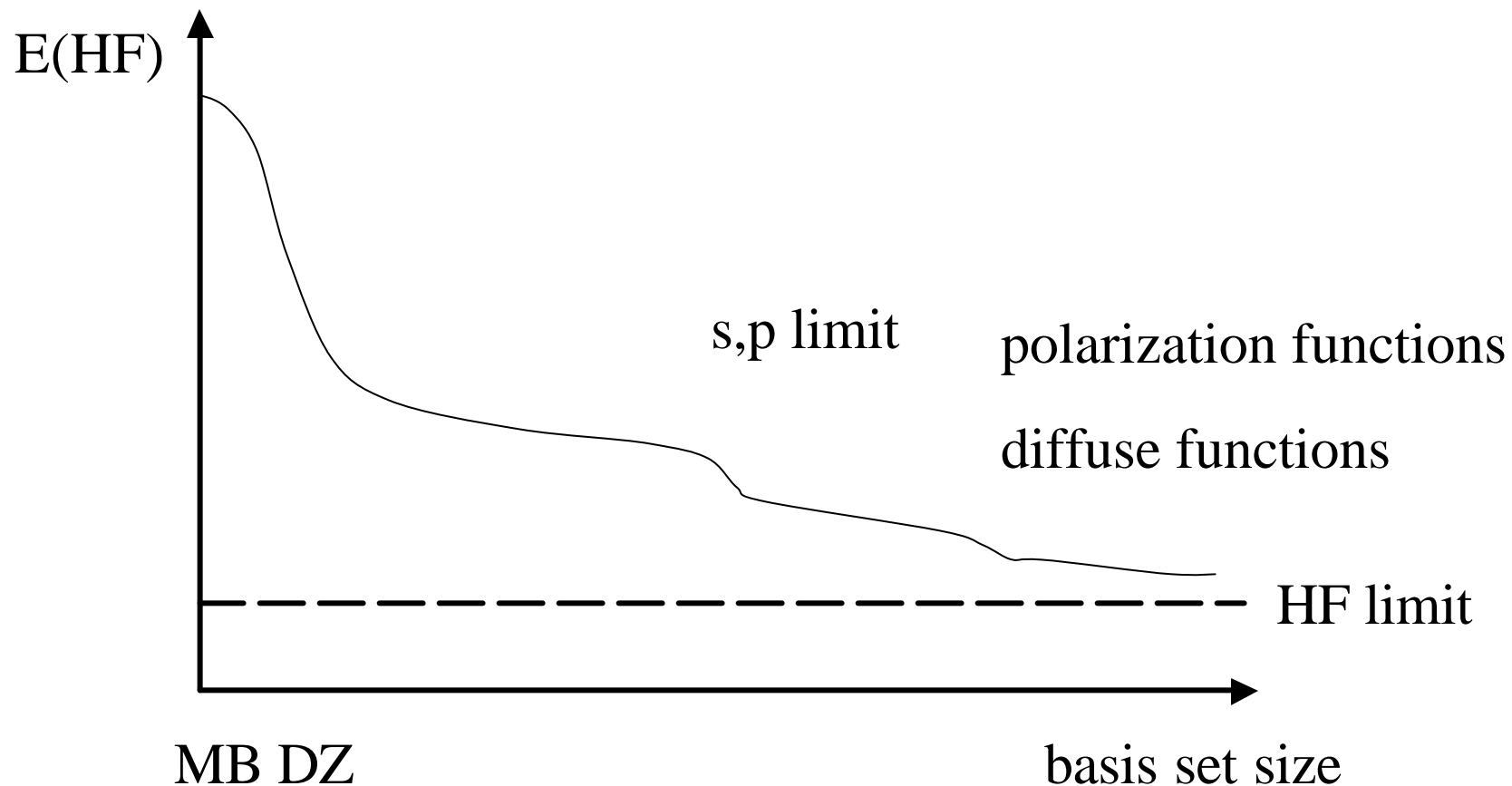
How does the inclusion of excited configurations describe electron correlation?

- A truly uncorrelated many-particle state is always represented by a product of one-particle functions (spin orbitals).
- Any superposition of such products represents a state where the motion of the particles is correlated.
- A SD is an antisymmetric superposition of spin-orbital products and it covers a major part of the correlation; That between electrons of equal spin – Fermi correlation.
- What we call electron correlation is the Coulomb correlation. This is not described by a single SD.
- In FCI one takes a linear combination of all determinants that can be constructed from the chosen one-electron basis.

- CI is an attempt to improve the wavefunction for a better description of the Coulomb correlation (covered by the dependence on the distance r_{12} in H) by allowing linear combinations of antisymmetrized products of one-electron functions.



- This is achieved by introducing more nodal surfaces that helps to keep the electrons separated.



Monte Carlo Configuration Interaction

- **Branching**
 - Random generation of S and D from a CI-vector
- **Pruning**
 - Disposal of CSFs according to their importance
- **Threshold parameter c_{\min}**
 - 10^{-2} , 10^{-3} , 10^{-4} corresponds to low, medium and high level of correlation

MCCI collects important configurations and works iteratively

1. Usually starts from the HF wavefunction

Take random sample of single and double excitations – 1st branching

New trial CI vector from “important” configurations – 1st pruning

2. Trial CI vector

Take random sample of single and double excitations from all the configurations in the CI vector

Keep the contributing configurations

Repeat until the energy does not change - convergence

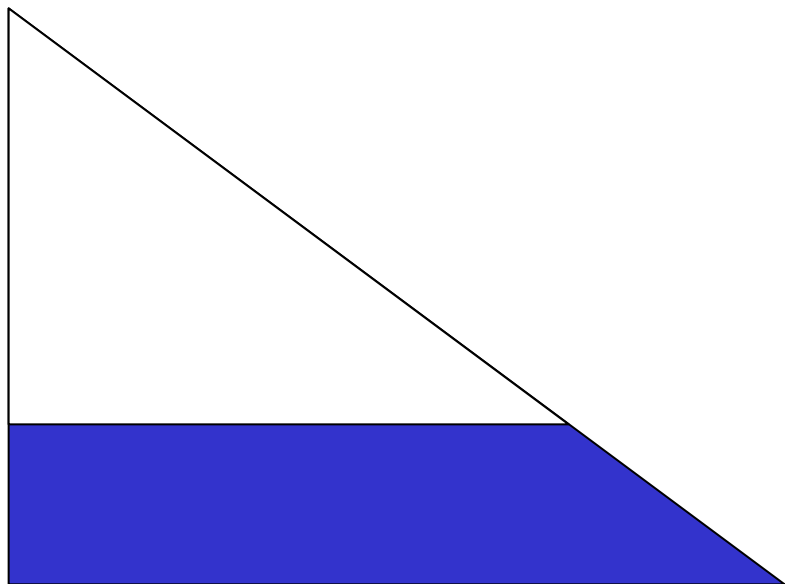
MCCI – not restricted to single reference

- Built in, automatic Multi-Reference character
- You need not know if a particular system requires MR
- You do not need to know which configurations should be included in your MR base

MCCI – not restricted to a certain level of excitations

- Does not stop at SD, SDT, SDTQ, etc. but does not include higher excitations if they are not important
- You need not know if a particular system requires triples or quadruples (or higher).
- Converges to FCI if c_{\min} is made smaller and smaller.

H matrix



CI vector prior to
branching

N new configurations
after branching

Accuracy and number of configurations

MCCI – on H₂O, dzp basis set

configurations = 56 million

FCI by Bauschlicher & Taylor in 1986

MCCI at $c_{\min} = 10^{-4}$ gives 99% of the FCI energy with a converged CI-vector only 3.1% of the FCI-vector length.

MCCI – on HF

configurations dz = 54 615

configurations dzp = 7 513 626

final MCCI vector = 1 710

final MCCI vector = 9 086

Linear vs. rectangular C_4

1988 Pacchioni & Koutecký

Method	winner	? E (meV)
SCF	L	204
SRCI	R	145
MRCI	L	106
Davidson	R	168

1991 Parasuk & Almlöf

MRCI	L	170
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1992 Watts et al

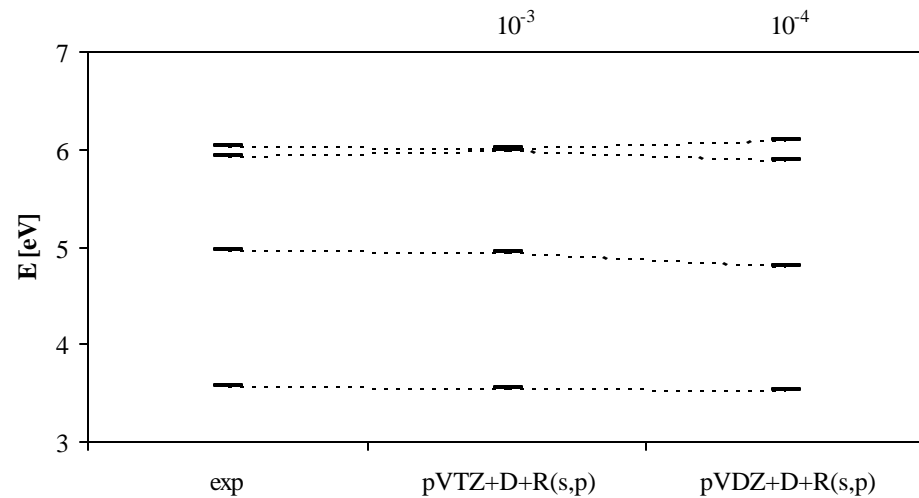
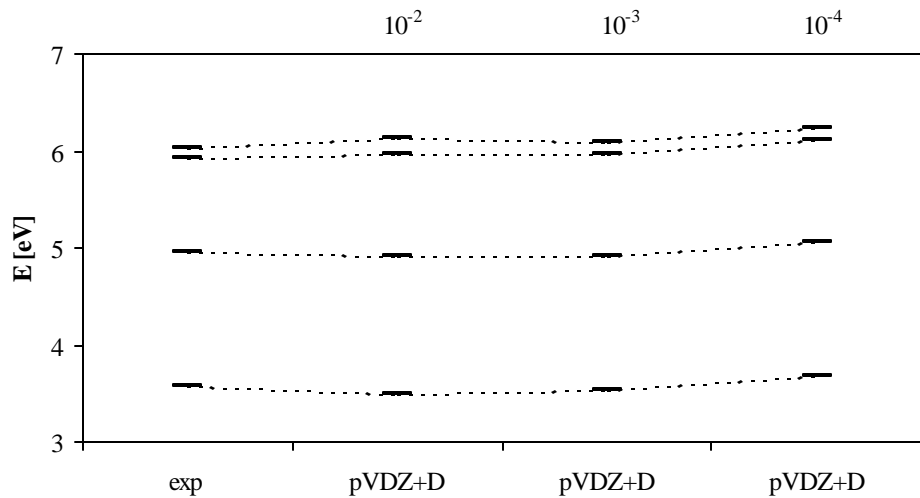
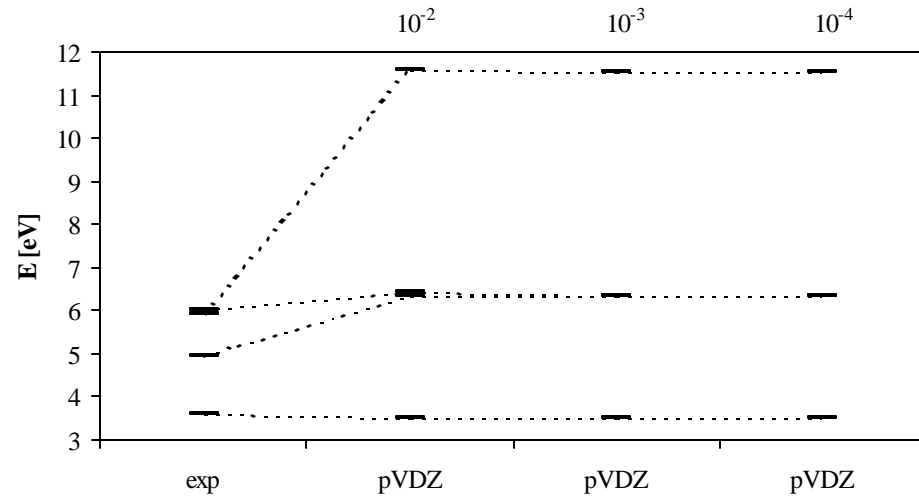
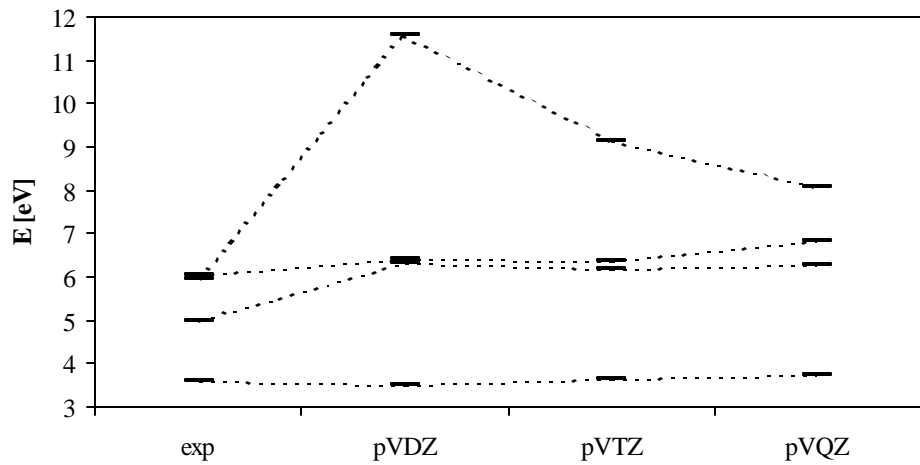
CCSD(T)/pVQZ	R	80
CCSD(T)/pVTZ	L	100

Greer?

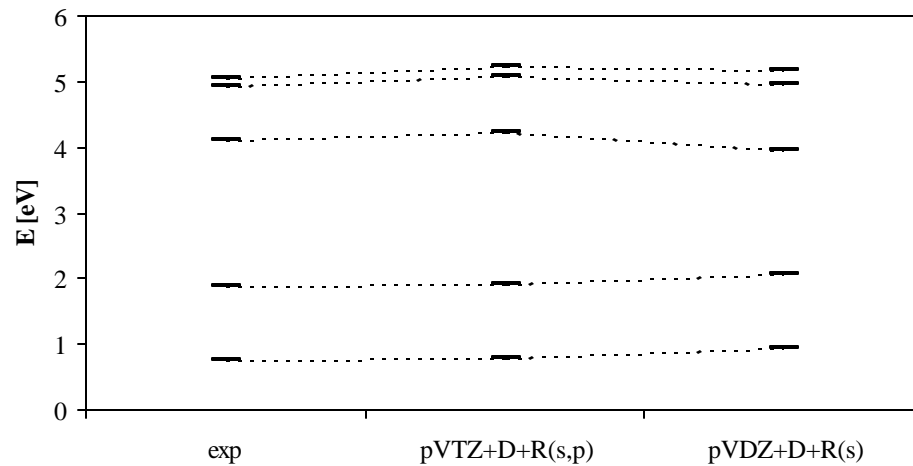
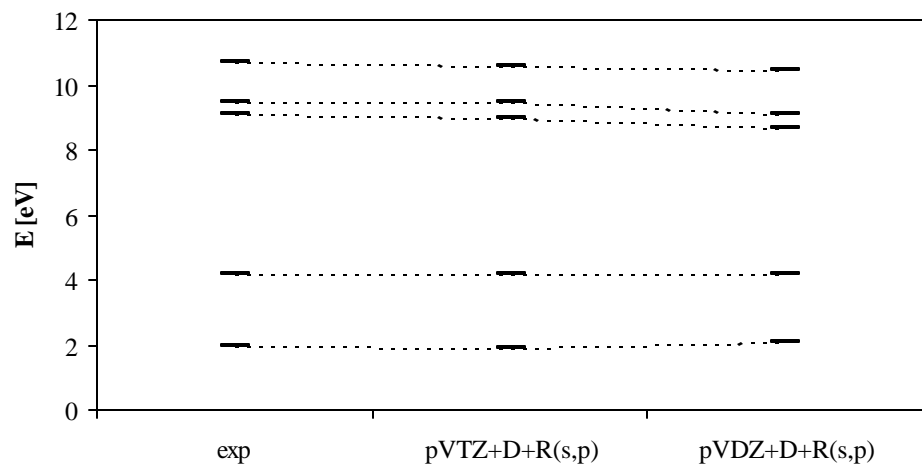
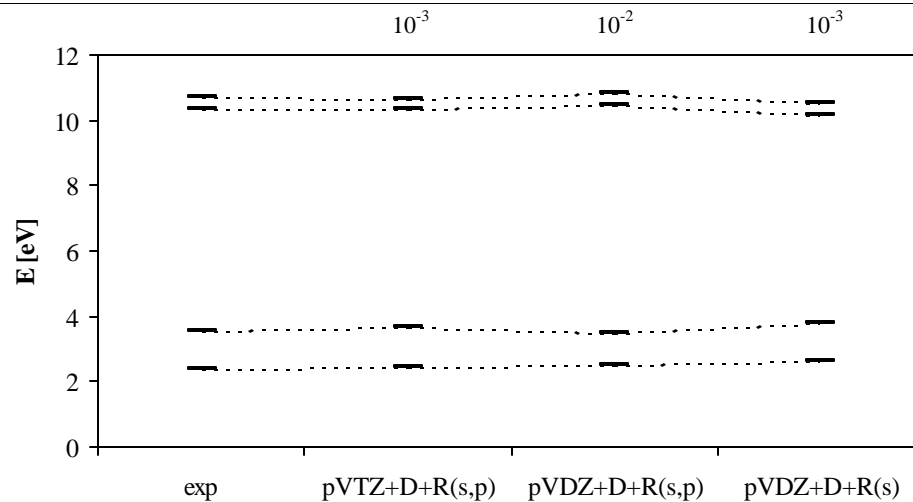
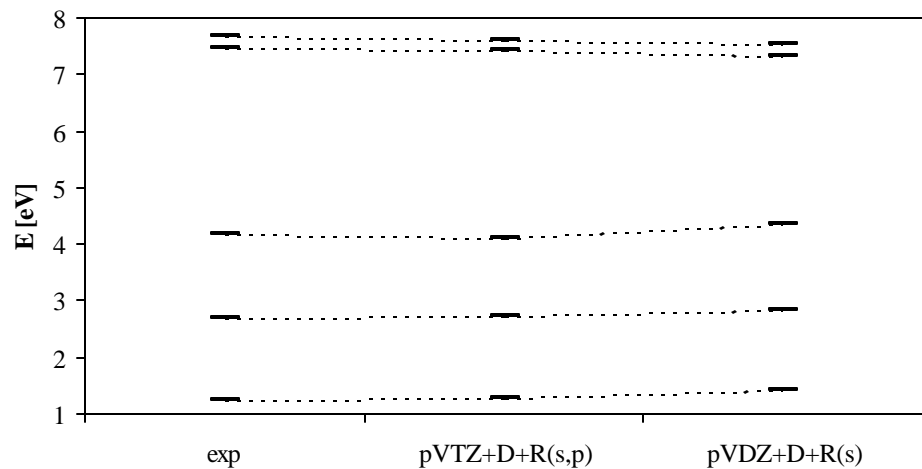
Excited states of atoms

- First row atoms B - Ne and Si.
- Lowest few excited states. Includes both valence and Rydberg states and a range of different multiplicities.
- Requirements on basis set.
- Level of electron correlation; the c_{\min} parameter.

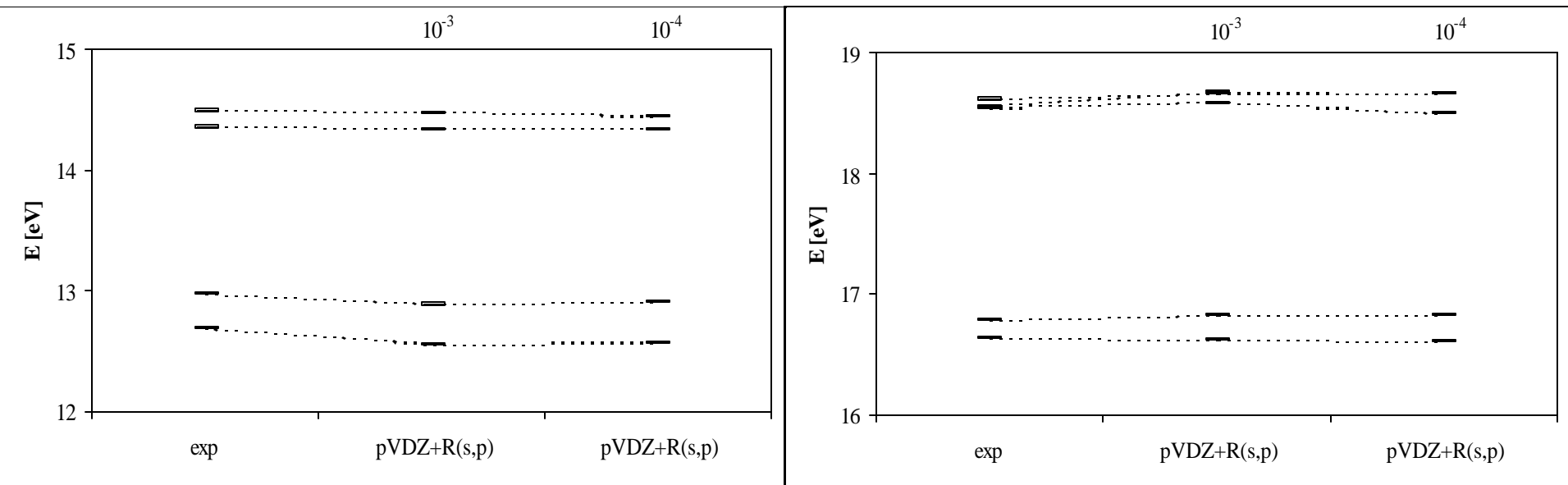
Boron, the test case



Carbon, nitrogen, oxygen, silicon



Fluorine and neon



Results for C, N, O, F, Ne and Si

Table II. Experimental and calculated values of the excited state energies relative to the ground states for the atoms C, N, O, F, Ne and Si. Excited state energies in eV and average error, $\overline{\Delta\Delta E}^a$ in meV. The electronic configurations and the term symbol for each excited state precedes the energies of each atom.

Atom	basis set ^b	c_{\min}^c	¹ D (2s ² 2p ²)	¹ S (2s ² 2p ²)	³ S (2s2p ³)	³ P (2s ² 2p3s)	¹ P (2s ² 2p3s)	$\Delta\Delta E$
C	experiment ^d		1.261	2.682	4.180	7.481	7.682	
	pVTZ+D+R(s,p)	10 ⁻³	1.291	2.722	4.097 ^e	7.438	7.622	51
	pVDZ+D+R(s)	10 ⁻³	1.439	2.835	4.347	7.317	7.528	163
N			² D (2p ³)	² P (2p ³)	⁴ P (2p ² 3s)	² P (2p ² 3s)		
	experiment ^d		2.384	3.576	10.331	10.685		
	pVTZ+D+R(s,p)	10 ⁻³	2.466	3.682	10.339	10.668		53
	pVDZ+D+R(s,p)	10 ⁻²	2.518	3.477	10.474	10.863		138
O			¹ D (2s ² 2p ⁴)	¹ S (2s ² 2p ⁴)	⁵ S (2s ² 2p ³ 3s)	³ S (2s ² 2p ³ 3s)	⁵ P (2s ² 2p ³ 3s)	
	experiment ^d		1.951	4.174	9.130	9.505	10.725	
	pVTZ+D+R(s,p)	10 ⁻³	1.938	4.200	9.007	9.498	10.567	65
	pVDZ+D+R(s,p)	10 ⁻³	2.066	4.215	8.665	9.114	10.457	256
F			⁴ P (2p ⁴ 3s)	² P (2p ⁴ 3s)	⁴ P (2p ⁴ 3s)	⁴ D (2p ⁴ 3s)		
	experiment ^d		12.701	12.980	14.361	14.508		
	pVDZ+R(s,p)	10 ⁻³	12.564	12.902	14.350	14.486		62
Ne			³ P (2p ⁵ 3s)	¹ P (2p ⁵ 3s)	³ S (2p ⁵ 3p)	³ S (2p ⁵ 3p)	¹ S (2p ⁵ 3p)	
	experiment ^d		16.645	16.782	18.547	18.565	18.625	
	pVDZ+R(s,p)	10 ⁻³	16.619	16.828	18.590	18.681	18.664	54
	pVDZ+R(s,p)	10 ⁻⁴	16.615	16.833	18.504	18.665	18.667	53
Si			¹ D (3s ² 3p ²)	¹ S (3s ² 3p ²)	⁵ S (3s3p ³)	³ P (3s ² 3p4s)	¹ P (3s ² 3p4s)	
	experiment ^d		0.769	1.896	4.119	4.922	5.070	
	pVTZ+D+R(s,p)	10 ⁻³	0.778	1.923	4.230	5.071	5.241	93
$\overline{\Delta\Delta E}$			0.955	2.062	3.960	4.973	5.192	137

- a) is defined to be the average over the number of states $|E_{\text{calc}}(\text{excited}) - E_{\text{calc}}(\text{ground}) - E(\text{exp})|$, where E_{calc} denotes the calculated total energy and E denotes the experimental transition energies.
- b) pVXZ denotes cc-pVXZ basis set, pVXZ+D denotes aug-cc-pVXZ basis set (X = D, T, Q) and R(s)/R(s,p) denotes the inclusion of 3s / 3s and 3p Rydberg functions (4s and 4p for Si).
- c) c_{\min} = minimum coefficient of configurations kept in the CI vector in the MCCI method.
- d) Experimental values from reference 12.
- e) Calculated with $c_{\min} = 10^{-4}$ and no frozen core electrons.

Recommended procedure

- Aug-cc-pVTZ+R(s,p) with $c_{\min} = 10^{-3}$ gives electronic transition within 100 meV.
- Aug-cc-pVDZ+R(s,p) with $c_{\min} = 10^{-2}, 10^{-3}$ gives accurate results for non-problematic cases.
- Rydberg functions can be left out of the basis set when non-Rydberg states are considered.

C-H and Si-H in GaAs

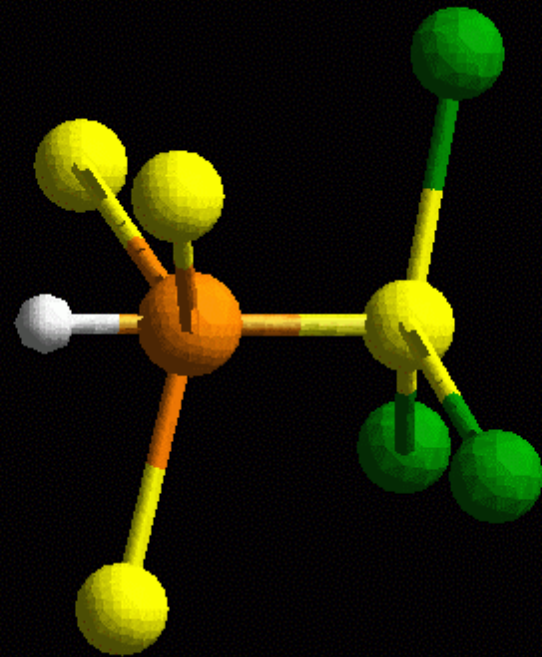
- Passivated dopant atoms - reliability and life-time.

Photo-assisted dissociation

- Silicon on gallium site → reactivation
- Carbon on arsenic site → no effect??

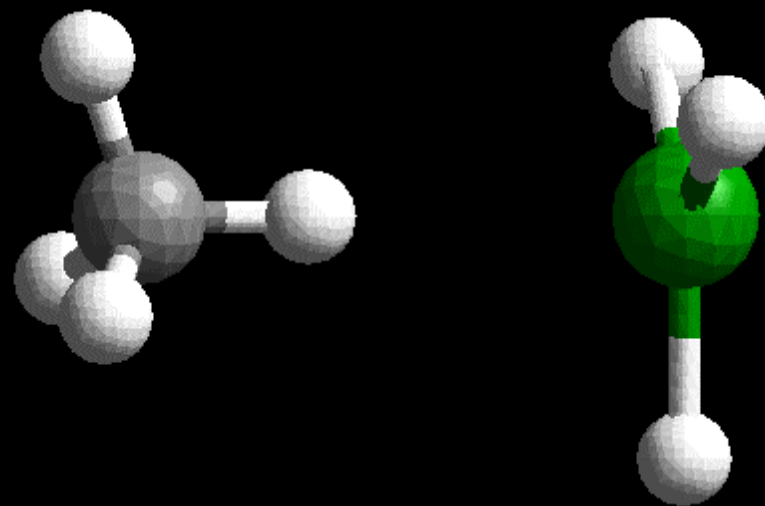
Hydrogen passivated Si_{Ga}

- H in “anti-bonding” interstitial position
- aug-cc-pVDZ basis. DZ on terminating H’s
- vertical excitation energy:
experiment 3.50 eV
 $c_{\min} = 10^{-2}$ 3.49 eV
 $c_{\min} = 10^{-3}$ 3.66 eV



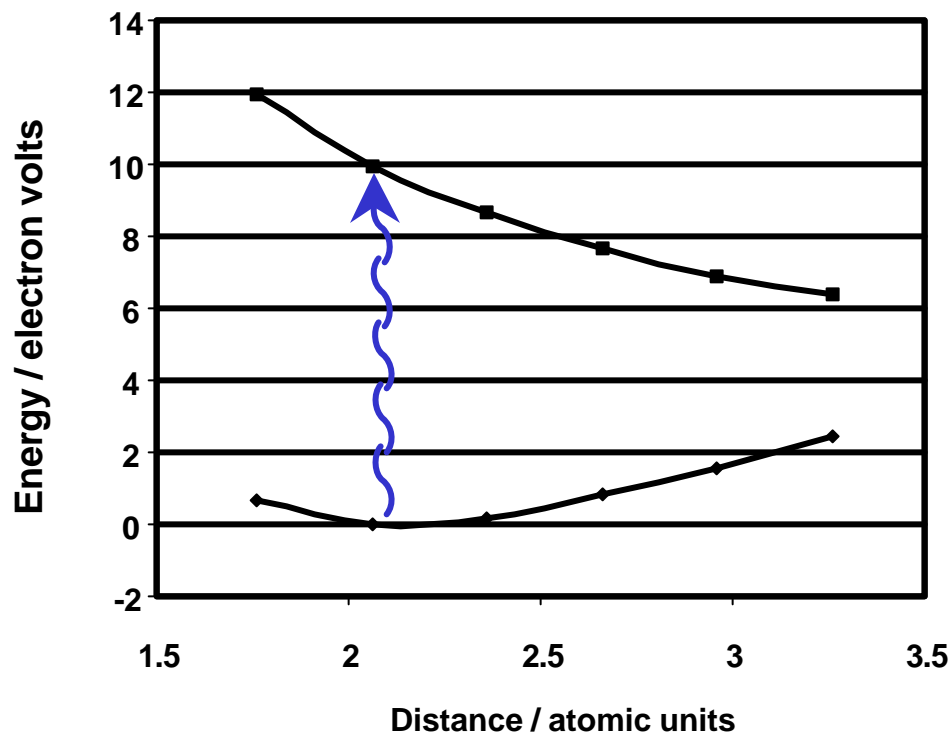
Hydrogen passivated C_{As}

- H between C and Ga
- Small cluster - no contributions from neighbouring atoms
- C -- Ga distance fixed to value from larger cluster
- aug-cc-pVDZ basis. DZ on terminating H's
- GS and ES potential energy surface



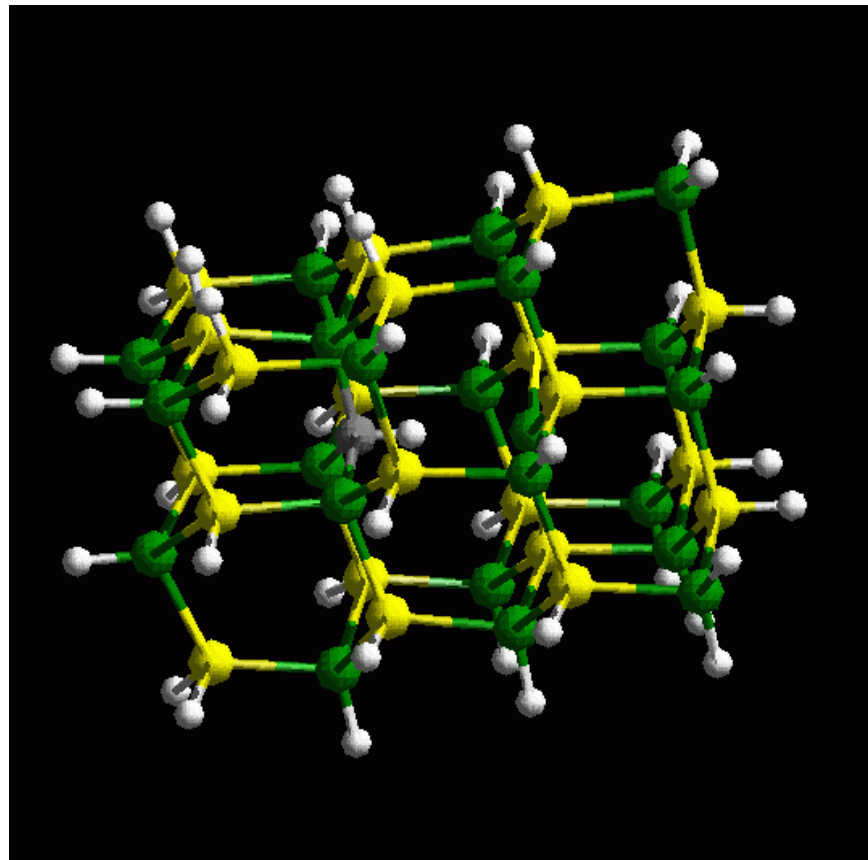
GS and ES PES for CH bond

- vertical excitation energy:
 $c_{\min} = 10^{-2}$ 9.93 eV
 $c_{\min} = 10^{-3}$ 10.02 eV
- ES surface is dissociative
but:
- Not accessible with
conventional spectro-
scopy tools (lasers).



$C_{As}H$ Excitation Energy

- More realistic description of the system.
- 87 atom cluster.
- 218 valence electrons, 46 active in excitation energy calculation.
- Vertical excitation energy
~ 6.0 eV.



Lowest doublet state of N@C₆₀

- CI on N@C₆₀ — 61 atoms, 245 e⁻
- 5 active electrons, — 2.867 eV c_{min} = 10⁻³
valence e⁻ of N
- 15 active electrons, — 2.889 eV c_{min} = 10⁻³
valence e⁻ of N plus
HOMO e⁻ of C₆₀

Electronic Excitations

Atomic Nitrogen

Endohedral Nitrogen

	Exp	Calc	Calculated
2D	2.384	2.624	2.867 eV
2P	3.576	3.805	3.968 eV

