Hierarchy of Gaussian Bases (5)

Split-valence bases that is VDZ, VTZ, etc. (e.g. Pople's bases 6-31G, 6-311G, etc.)

Polarized split-valence bases VDZP, VTZP, etc.

Dunning's bases (correlation consistent) cc-pVXZ, $X=D, T, Q$,5,6,...

- basis cc-pVDZ is the VDZP $3s2p1d$ for Li through Ne
- basis cc-pV(X+1)Z contains for each l one extra basis function compared to cc-pVXZ
- bases cc-pVTZ and cc-pVQZ are of the following composition $4s3p2d1f$ i $5s4p3d2f1g$
- bases aug-cc-pVXZ contain one extra function with small exponent ("diffuse function") for each l
- bases d-aug-cc-pVXZ contain two extra functions with small exponent ("diffuse functions") for each l

Bases aug-cc-pVXZ and d-aug-cc-pVXZ are employed in calculations of polarizabilities and intermolecular interactions

Dunning's bases permit an extrapolation of the results of finite basis set calculations to the results corresponding to the complete (infinite) basis

Correlation-consistent basis sets

	H-He	Li-Ne	Na-Ar
cc-pVDZ	[2*s*1*p*] → 5 func.	[3*s*2*p*1*d*] → 14 func.	[4*s*3*p*1*d*] → 18 func.
cc-pVTZ	[3*s*2*p*1*d*] → 14 func.	[4*s*3*p*2*d*1*f*] → 30 func.	[5*s*4*p*2*d*1*f*] → 34 func.
cc-pVQZ	[4*s*3*p*2*d*1*f*] → 30 func.	[5*s*4*p*3*d*2*f*1*g*] → 55 func.	[6*s*5*p*3*d*2*f*1*g*] → 59 func.

To understand how to get the number of functions take the cc-pVDZ basis set for H: There are two *s* ($L = 0$) orbitals and one *p* ($L = 1$) orbital that has 3 components along the z-axis ($m_L = -1,0,1$) corresponding to p_x, p_y and p_z. Thus, five spatial orbitals in total. Note that each orbital can hold two electrons of opposite spin.

Dunning's bases. CBS extrapolations

Dunning bases permit a Complete Basis Set (CBS) extrapolation. This is a result of the systematic (monotonic) dependence of the energy on X (Dunning bases up to octuple zeta X=8 were developed).

In correlation energy calculations one usually assumes the following extrapolation formula

$$E(X) = E(\infty) + A\,X^{-3}$$

Adjusting A and the CBS limit, $E(\infty)$, using two consecutive energies (computed for X and X-1) we get:

$$E(\infty) = E(X-1) + \frac{E(X) - E(X-1)}{1-(1-1/X)^3}$$

When $X \geq 4$ such a two-pint extrapolation usually gives very good results.

Three-point extrapolation procedures, based on the formulas are also used.

$$E(X) = E(\infty) + A\,X^{-\alpha} \qquad \text{lub} \qquad E(X) = E(\infty) + Ae^{-\alpha X}$$

In SCF theory the latter method - the exponential extrapolation is better.

Electron correlation

The name "electron correlation" comes from probability theory and statistics. Random variables x and y are independent if the probability density factorizes

$$\rho(x, y) = \rho_1(x)\, \rho_2(y)$$

This means that the conditional probability

$$\rho(x|y_0) = \frac{\rho(x, y_0)}{\int \rho(x, y_0) dx} = \rho_1(x)$$

is independent of y_0.

When these conditions are not satisfied the random variables are correlated.

Example of independent variables: velocity components v_x, v_y, v_z of a molecule in a fluid of temperature T (Maxwell distribution):

$$\rho(v_x, v_y, v_z) \sim e^{-m(v_x^2+v_y^2+v_z^2)/2kT} \sim e^{-mv_x^2/2kT}\, e^{-mv_y^2/2kT}\, e^{-mv_z^2/2kT}$$

Example of dependent variables: coordinates x, y and z of the electron in a hydrogen atom:

$$\rho(x, y, z,) = |\psi(x, y, z,)|^2 = \frac{1}{\pi} e^{-2\sqrt{x^2+y^2+z^2}}$$

Electron correlation, helium atom

Coordinates of electron 1 and electron 2 in the helium atom are random variables. Are they correlated? The answer is given by the square of the wave function $|\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2)|^2$ (integrated over spin).

In the Hartree-Fock theory (RHF) $\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = |\psi\alpha\ \psi\beta|$. The probability density $\rho(\vec{r}_1, \vec{r}_2)$ takes then the form:

$$\rho(\vec{r}_1, \vec{r}_2) = |\psi(\vec{r}_1)|^2\, |\psi(\vec{r}_2)|^2 = \rho(\vec{r}_1)\, \rho(\vec{r}_2)$$

In the case of the exact wave function this identity does not hold.

The density $\rho(\vec{r}_1, \vec{r}_2)$ does not factorize because the electrons repel each oder

For the helium atom the effect of this correlation is not large:

	SCF	Schrödinger	error
total energy	-2.8617	-2.9037	1.5%
ionization potential	0.8617	0.9037	4.9%

In atoms we distinguish the radial correlation and angular correlation.

Electron correlation, linear molecules

For molecules the correlation error in the total energy E (in hartree) is small:

Molecule	SCF	Schrödinger	error
H_2	-1.134	-1.174	-3.4%
Li_2	-14.872	-14.994	-0.8%
N_2	-108.996	-109.586	-0.6%
F_2	-198.768	-199.670	-0.5%

but error in the electronic binding energy D_e (given in eV) is very large:

Molecule	SCF	Schrödinger	error
H_2	3.65	4.75	-23%
Li_2	0.17	1.05	-84%
N_2	5.27	9.90	-47%
F_2	-1.37	1.68	-182%

Electron correlation, linear molecules, continued

In linear molecules we have the following kinds of correlation:

- angular correlation
- radial correlation (“in-out”)
- “left-right” correlation

The missing “left-right” correlation has the unpleasant consequence that:

The RHF method is not size consistent

An electronic structure method is size-consistent (extensive) if

$$\lim_{R\to\infty} E(\mathrm{A{-}B}) = E(\mathrm{A}) + E(\mathrm{B})$$

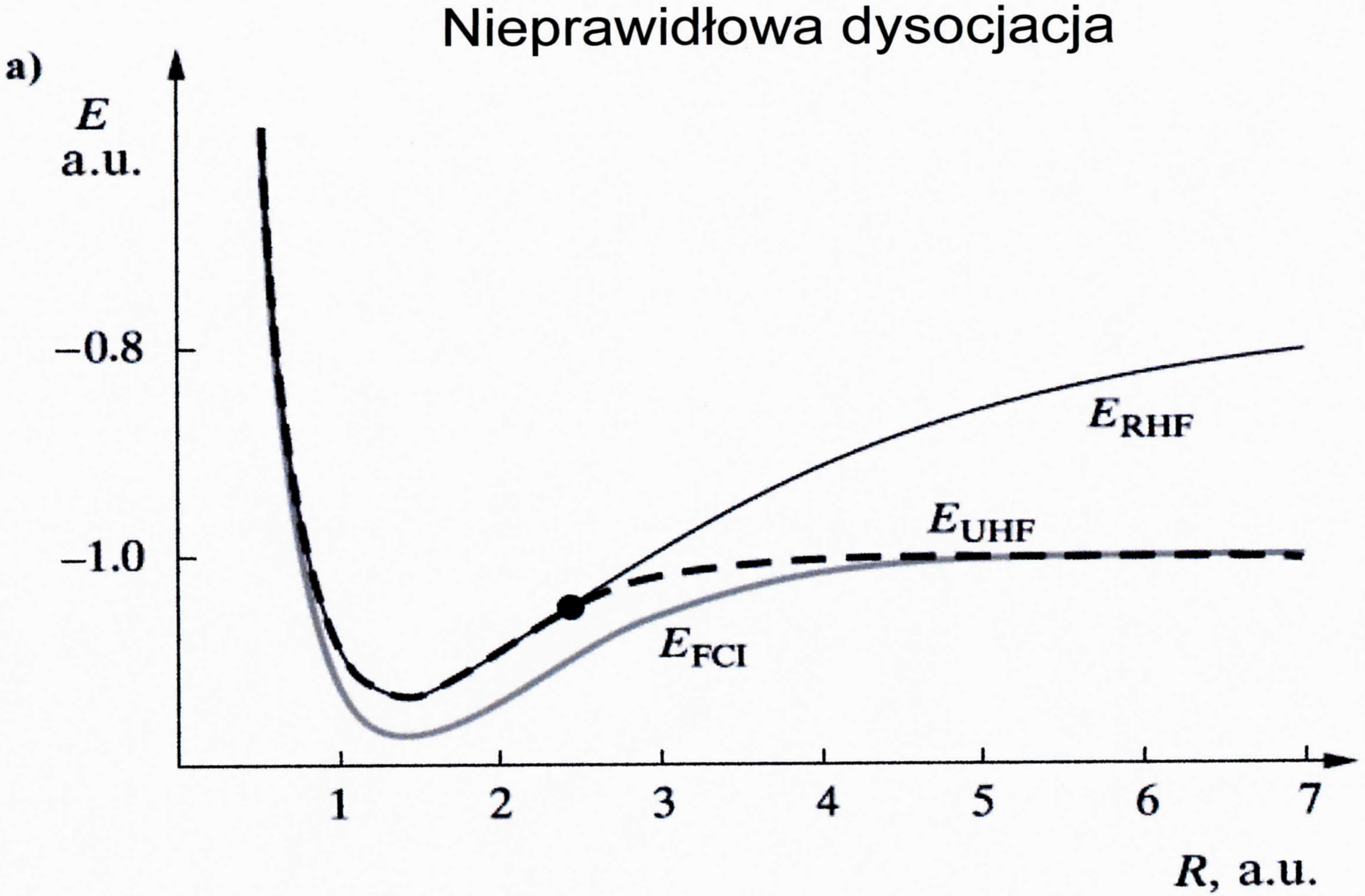
where $E(\mathrm{A{-}B})$, $E(\mathrm{A})$, i $E(\mathrm{B})$ are results of calculations for the dimer A−B and for the monomers A i B, respectively.

The UHF method is size consistent

Strictly speaking the HF method accounts for the so called Fermi correlation but always neglects the Coulomb correlation.

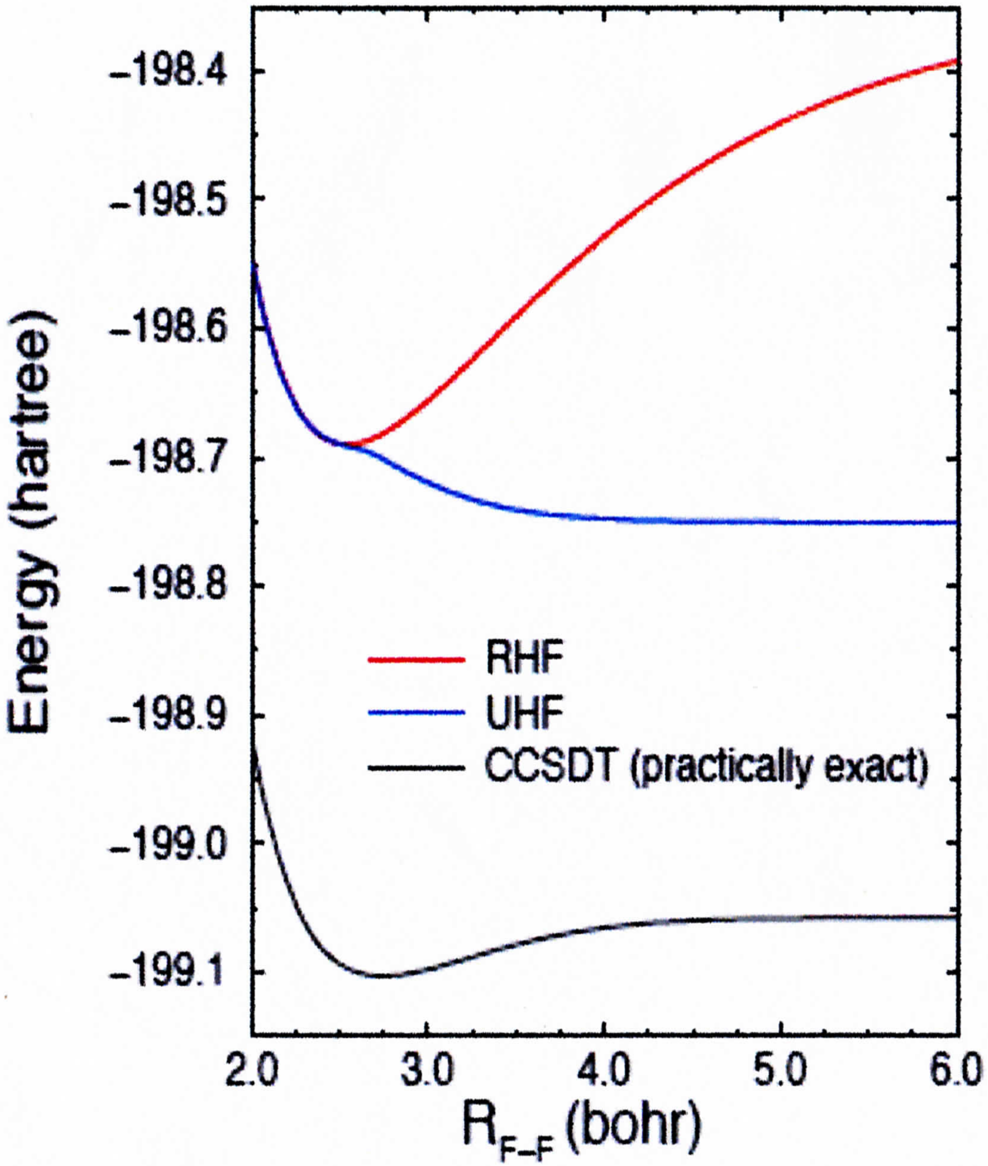
Definition of the correlation energy $E_{\mathrm{corr}} = E_{\mathrm{HF}} - E_{\mathrm{exact}}$

Potential energy curves for the hydrogen molecule



ELECTRONIC STRUCTURE:

Bond breaking in F_2



Strong points of the Hartree-Fock method

Despite the problems mentioned earlier the HF theory has many strong points:

- Simplicity. The time of conventional calculations scales as M^4, but a linear scaling is feasible with a good control of accuracy
- The HF method is good for the calculations of:
  - molecular geometries (bond lengths and angles between bonds)
  - electron densities (dipole moments)
  - energies of hydrogen bonds
  - energies of conformation changes
  - energies of isodesmic reactions
- Less accurate but reasonably accurate are:
  - geometries of transition states (saddle points)
  - polarizabilities
  - force constants
  - shielding constants (NMR)
  - energies of reactions with closed-shell reagents and products
- Time-dependent HF theory (TDHF theory) gives often a possibility to estimate the energies of simple electronic excitations
- Results of HF calculations are used as a starting point in correlation energy calculations

Serious problems of the Hartree-Focka theory

- Very inaccurate or completely wrong dissociation energies
- Inaccurate activation barriers (reaction barriers)
- completely wrong interaction energies of atoms and non-polar molecules
- Inaccurate higher polarizabilities (hyperpolarizabilities)
- Wrong cohesive energies of metals
- Breaking of spin and spatial symmetry
- Even when the HF method works the results are never very accurate

Major techniques of including the electron correlation

- Method of explicitly correlated bases (depending explicitly on $r_{ij}=|\vec{r}_i-\vec{r}_j|$)
- Methods using the orbital expansion (about 10% of all calculations)
- Density functional method– DFT method (about 90% of all calculations)
- Quantum Monte Carlo method (QMC)