

Quantum Chemistry

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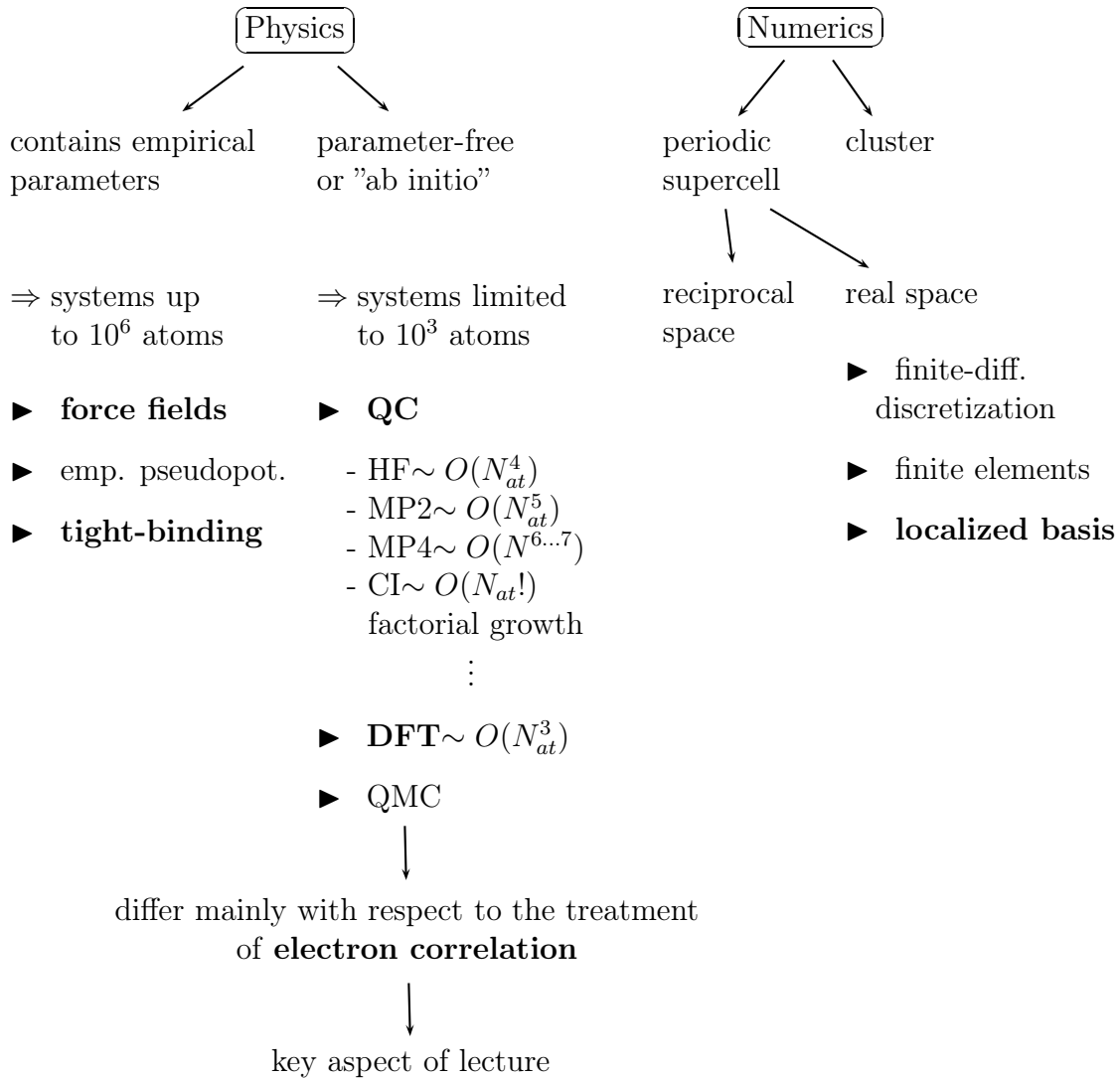
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0. Introduction

0.1. Methods of Computational Materials Science



0.2. Atomic Units

Schrödinger Equation (SE) in SI units for H atom

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi = E\psi$$

to cast this equation into dimensionless form we let $x, y, z \rightarrow \lambda x', \lambda y', \lambda z'$ and obtain

$$\left\{ -\frac{\hbar^2 \nabla'^2}{2m_e \lambda^2} - \frac{e^2}{4\pi\epsilon_0 \lambda r'} \right\} \psi' = E\psi'$$

choose λ such that

$$\frac{\hbar^2}{m_e \lambda^2} = \frac{e^2}{4\pi\epsilon_0 \lambda} = \epsilon_a : \text{atomic unit of energy called "Hartree"}$$

$$\Rightarrow \lambda = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0 : \text{"Bohr radius"}$$

$$\Rightarrow \epsilon_a \left\{ -\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right\} \psi' = E\psi'$$

with $E' = \frac{E}{\epsilon_a}$ we obtain dimensionless equation

$$\left\{ -\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right\} \psi' = E'\psi'$$

→ SE in atomic units, solution of this equation for atomic hydrogen yields $E' = -0.5$

$$1 \text{ Hartree} = 27.211 \text{ eV}$$

$$1 a_0 \text{ (bohr)} = 0.52918 \text{ \AA}$$

1. The adiabatic and Born-Oppenheimer Approximations

$$H\psi = E\psi$$

$$H = T_n + T_e + V_{ne} + V_{ee} + V_{nn}$$

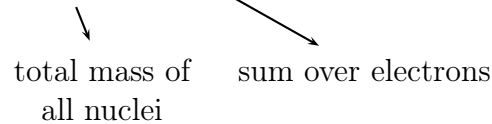
⇒ transformed to the center of mass system

$$H = T_n + H_e + H_{mp}$$

with

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn} : \text{ electronic Hamiltonian}$$

$$H_{mp} \sim \frac{1}{2M_{tot}} \left(\sum_{i=1}^N \nabla_i \right)^2 : \text{ mass polarization}$$



 total mass of all nuclei sum over electrons

$\psi_i(R, r)$: full set of solutions to the electronic SE

R : nuclear positions

r : electronic positions

$$H_e(R)\psi_i(R, r) = E_i(R)\psi_i(R, r) \quad i = 1, 2, \dots$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}, \quad \text{complete set}$$

expand total wave function

$$\psi_{tot}(R, r) = \sum_{i=1}^{\infty} \psi_{ni}(R)\psi_i(R, r)$$

inserting into the SE gives

$$\sum_i (T_n + H_e + H_{mp})\psi_{ni}(R)\psi_i(R, r) = E_{tot} \sum_i \psi_{ni}(R)\psi_i(R, r)$$

with $T_n = \sum_a -\frac{1}{2M_a} \nabla_a^2 =: \nabla_n^2$

$$\sum_i \{ \nabla_n^2 (\psi_{ni}\psi_i) + H_e\psi_{ni}\psi_i + H_{mp}\psi_{ni}\psi_i \} = E_{tot} \sum_i \psi_{ni}\psi_i$$

H_e and H_{mp} only act on the electronic wave function and ψ_i is exact solution to electronic SE

$$\sum_i \left\{ \psi_i (\nabla_n^2 \psi_{ni}) + 2(\nabla_n \psi_i)(\nabla_n \psi_{ni}) + \psi_{ni} (\nabla_n^2 \psi_i) + \psi_{ni} E_i \psi_i + \psi_{ni} H_{mp} \psi_i \right\} = E_{tot} \sum_i \psi_{ni} \psi_i$$

$$\left| \int \psi_j^*(R, r) d^3r, \quad \text{use orthonormality} \right.$$

$$\nabla_n^2 \psi_{nj} + E_j \psi_{nj} + \sum_i \left\{ \underbrace{2 \langle \psi_j | \nabla_n | \psi_i \rangle (\nabla_n \psi_{ni})}_{\text{first-order non-adiabatic coupling element}} + \underbrace{\langle \psi_j | \nabla_n^2 | \psi_i \rangle \psi_{ni}}_{\text{2nd order non-adiabatic coupling elements}} + \langle \psi_j | H_{mp} | \psi_i \rangle \psi_{ni} \right\} = E_{tot} \psi_{nj}$$

non-adiabatic coupling elements important for systems involving more than one electronic surface (e.g. photochemical reactions)

Adiabatic approx.: neglect coupling in the above equation, only the terms with $i = j$ survive

Remark

- ▶ often even more stringent: only ground state $i = 0$ is considered in adiabatic approximation

$\Leftrightarrow e^-$ adjust instantaneously to actual nuclear configurations, even when nuclei are rapidly moving, e^- occupies only ground state
 diagonal first-order non-adiabatic coupling element is zero

\Rightarrow SE in adiabatic approx.

$$\left\{ \nabla_n^2 + E_j + \langle \psi_j | \nabla_n^2 | \psi_j \rangle + \langle \psi_j | H_{mp} | \psi_j \rangle \right\} \psi_{nj} = E_{tot} \psi_{nj}$$

mass polarization of the order of relativistic effects (that are neglected anyway)

⇒ neglect H_{mp}
 [N. Yamanaka, *J. Phys. B.* **32**, 1597 (1999)]

$$\Rightarrow \left\{ T_n + E_j + \underbrace{\langle \psi_j | \nabla_n^2 | \psi_j \rangle}_{U(R)} \right\} \psi_{nj} = E_{tot} \psi_{nj}$$

$U(R)$: diagonal correction
 $\frac{U}{E_j} \approx \frac{m}{M}$

+ usually slowly varying function of R

⇒ shape of energy surface is therefore determined almost exclusively by $E_i(R)$

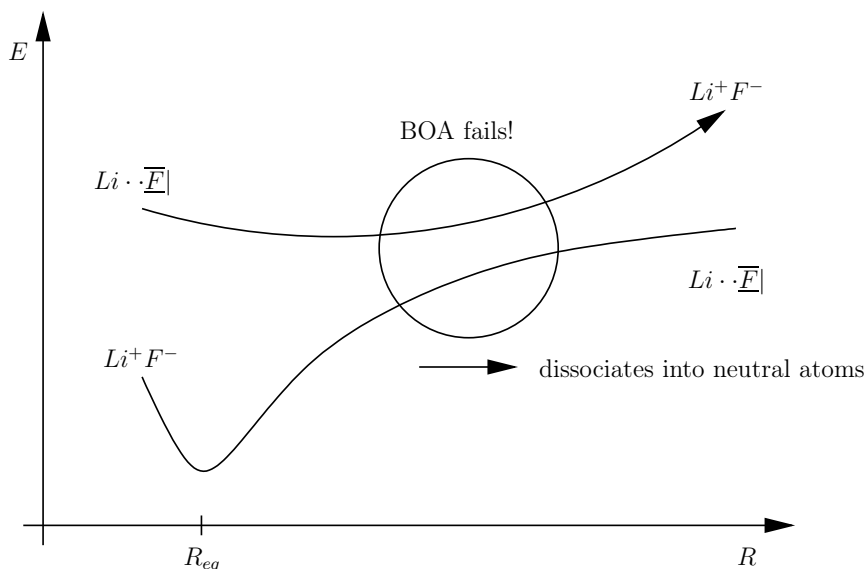
Born-Oppenheimer (BO) approximation:

neglect diagonal correction

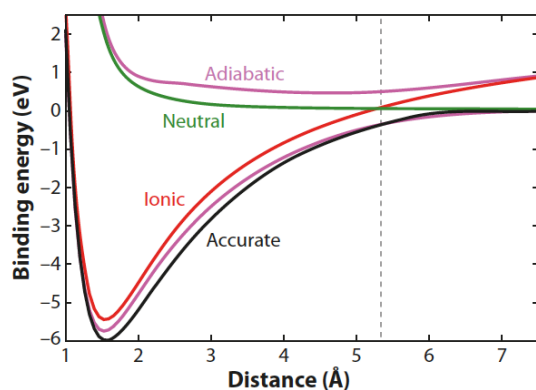
$$\left\{ T_n + \underbrace{E_j(R)}_{=V_j(R)} \right\} \psi_{nj}(R) = E_{tot} \psi_{nj}(R)$$

Remarks

- ▶ in the BOA nuclei move on a potential energy surface (PES) which is a solution to the electronic SE
- ▶ ⇒ molecular vibrations & rotations
- ▶ concepts of eq. & transition state geometries (critical points on PES)
- ▶ BOA usually good, breaks down when two (or more) solutions to the electronic SE come close together energetically

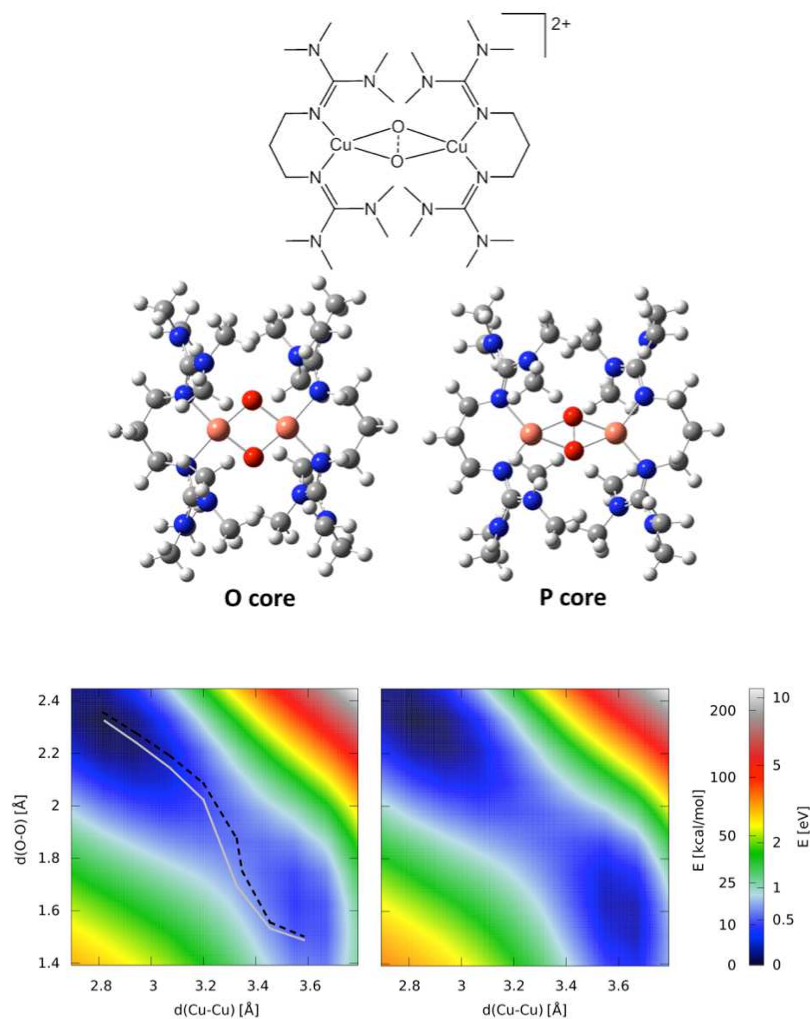
Example: LiF

Wave function at long distances of covalent type, for shorter distances the ground state is ionic, i.e., the adiabatic states change their character during the dissociation. Alternatively, the system can be described using diabatic ionic and covalent (neutral) states that maintain the same character and cross at the capture radius for Li^+F^- .



Dissociation curves of LiF with various approximate methods, adapted from *T. Van Voorhis et al., The diabatic Picture of Electron Transfer, Reaction Barriers, and Molecular Dynamics, Annu. Rev. Phys. Chem.* 61, 149 (2010).

The potential energy surface (PES) may be far more complicated for complex structures. Shown below are two metastable configurations for a biometric model complex for tyrosinase and the corresponding calculated Cu_2O_2 core PES. The calculations were performed for closed-shell configuration with PW91/plane waves (left) and B3LYP/cc-pVDZ (right). From *M Rohrmüller, A Hoffman, C Thierfelder, S Herres-Pawlis, WG Schmidt, J. Comput. Chem.* 36, 1672 (2015).



Once the BOA is made, the problem reduces to solving the electronic SE for a set of nuclear geometries

2. Force Field Methods

Last chapter: one of the major problems is calculating the electronic energy for a given configuration

⇒ bypass this step, consider E_0 as a parametric function of the nuclear coordinates

Why?

- proteins
- solvents
- hybrid methods

Approach: Molecules → modelled as atoms held together by bonds

⇔ "ball & spring" model

⇔ "Molecular Mechanics (MM)" method

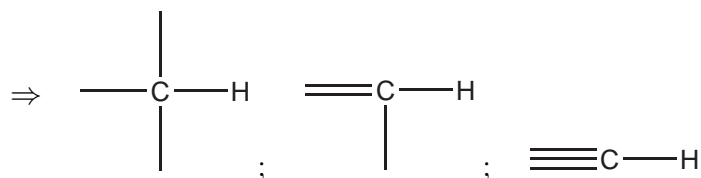
Basis assumption: molecules tend to be composed of units (functional groups) which are structurally similar in different molecules

Example: C–H bond

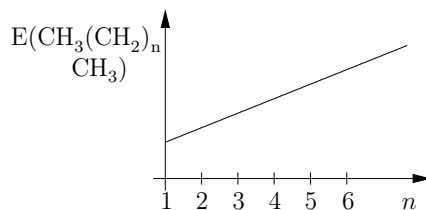
$$d_{eq} = 1.06 \dots 1.10 \text{ \AA}$$

$$\text{vibrations } 2900 \dots 3300 \text{ cm}^{-1}$$

⇒ reduce variation by classifying the C–H bonds according to the coordination of C, i.e.



similar observation for energy



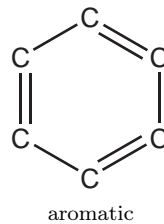
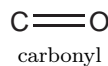
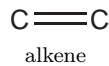
⇒ each CH_2 group contributes essentially the same amount of energy

⇒ "atom types", atom type depends on the atomic number and the type of chemical bonding it is involved in

Example: MM2

▶ sp^3 -hybridized carbon → Type 1

▶ sp^2 -hybridized carbon → Type 2, 3, 50



2.1. Force Field Energy

$$E_{FF} = E_{Str} + E_{bend} + E_{tors} + E_{vdW} + E_{el} + E_{cross}$$

Stretch Energy:

$$E_{Str} \underbrace{(R^{AB} - R_0^{AB})}_{\Delta R^{AB}} = \underbrace{E(0)}_{:=0} + \underbrace{\frac{dE}{dR}}_{=0} \Delta R^{AB} + \frac{1}{2} \frac{d^2E}{dR^2} (\Delta R^{AB})^2$$

$$:= K_2^{AB} (\Delta R^{AB})^2$$

usually sufficient for determination of equilibrium energy

need to do better for some (strained) systems & vibrational frequencies

⇒ straight forward to include more terms

$$E_{Str}(\Delta R^{AB}) = K_2^{AB} (\Delta R^{AB})^2 + K_3^{AB} (\Delta R^{AB})^3 + \dots$$

Problem: polynomial expansions do not have the correct limiting behaviour

⇒ molecule may fly apart, or energy goes to infinity

⇒ **Morse potential** [P.M. Morse, PR 34, 57 (1929)]

$$E_{Morse}(\Delta R) = D [1 - e^{-\alpha \Delta R}]^2$$

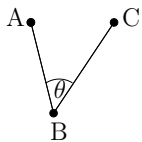
D : dissociation energy

$$\alpha = \sqrt{\frac{K}{2D}}, \quad K : \text{force constant}$$

Problem: restoring force for long bonds small

⇒ At least two parameters for E_{Str}
 K^{AB} & R_0^{AB}
 in case of Morse we also need α or D

Bending Energy:



$$E_{bend} (\theta^{ABC} - \theta_0^{ABC}) = K^{ABC} (\theta^{ABC} - \theta_0^{ABC})^2$$

usually sufficient for up to $\pm 30^\circ$

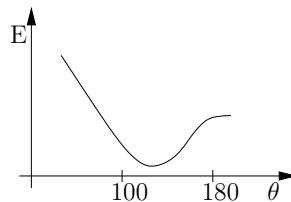
for higher bending angles we take higher order coefficients

Remarks

- ▶ di-or trivalent central atom
 ⇒ must have max. of energy for

$$\theta^M \left(\left. \frac{dE}{d\theta} \right|_{\theta^M} = 0; \quad \left. \frac{d^2E}{d\theta^2} \right|_{\theta^M} < 0 \right)$$

Example: H₂O



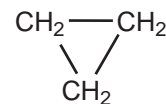
- ▶ special atom types for small rings

Example: Cyclopropane

sp^3 -hybridized, but

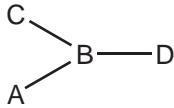
$$\theta_0^{ccc} = 60^\circ$$

(instead of 110° in acyclic system)



► out-of-plane bending energy

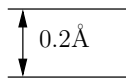
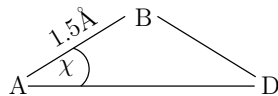
Example:



$$\sum \theta_i = 360^\circ$$

B sp^2 -hybridized

high energy costs for destroying planarity



$$\Rightarrow \sum \theta_i = 354.8$$

should not translate out-of-plane bending in bending energy of XY angle, better to introduce new angle χ

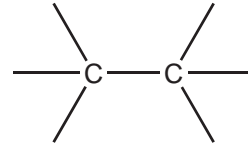
$$E_{oop}(\chi^B) = k^B(\chi^B)^2$$

otherwise molecule becomes too stiff

Torsional Energy:

Example: ethane

3 eclipsed conformations \rightarrow 3 maxima of E_{tor}
 3 staggered conformations \rightarrow 3 minima of E_{tor}



need periodic function of the energy (in particular since the energy cost of rotations is usually small $\rightarrow \Delta w$ large)

$$\Rightarrow E_{tors}(w) = \sum_{n=1} V_n \cos(nw)$$

van der Waals Energy:

[*"dispersion" or "London" force, F. London, Z. Phys. 63, 245 (1930)*]

$$E_{vdW}(R^{AB}) = E_{repulsive}(R^{AB}) - \frac{C^{AB}}{(R^{AB})^6}$$

$E_{repulsion}(R \rightarrow 0) \rightarrow \infty$
 $(R \rightarrow \infty) \rightarrow 0$ (faster than R^{-6})

functional form not known

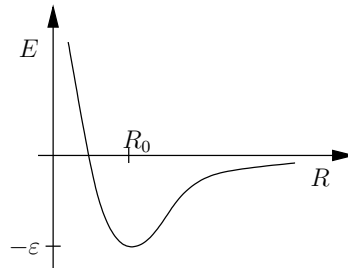
popular potential that obeys these general requirements is Lennard-Jones (LJ) potential

[*J. E. Lennard-Jones, Proc. R. Soc. London, Ser. A, 106, 463 (1924)*]

$$E_{LJ}(E) = \frac{C_1}{R^{12}} - \frac{C_2}{R^6}$$

often written as

$$E_{LJ}(R) = \varepsilon \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right]$$



- ▶ no theoretical (or exp.) arguments for 12th power!
- ▶ repulsion due to overlap of electronic wave functions
- ▶ electron density falls off exponentially (at least for H atom)

⇒ "Hill" type potential or "Exp.-6" potential

$$E_{vdW}(R) = \varepsilon \left[\frac{6}{\alpha - 6} e^{\alpha \left(1 - \frac{R}{R_0}\right)} - \frac{\alpha}{\alpha - 6} \left(\frac{R_0}{R} \right)^6 \right]$$

α : free parameter

[*T. L. Hill, J. Chem. Phys. 16, 399 (1948)*]

problem with small R

exp. term \rightarrow const.

$-R^{-6} \rightarrow -\infty$

⇒ nuclear fusion for too short bond lengths!

⇒ Morse potential $E = D [1 - e^{-\alpha(R-R_0)}]^2$

$$D_{vdw}, \alpha_{vdW} \ll D_{cov}, \alpha_{cov}$$

Quality: 1) Morse
 2) Exp-6
 3) LJ

[*J. R. Hart and A. K. Rappe, J. Chem. Phys.* **97**, 1109 (1992)]

Nevertheless, most force fields employ LJ!

Why?

$$R_{i,j} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

numerical effort $\mathcal{O}(\sqrt{\cdot}, exp) \sim 5\mathcal{O}(*, +)$

need no R in LJ, just R^6 (and $(R^6)^2$)!

\Rightarrow reason for R^{-12} repulsion,
 $R^{-9\dots 10}$ gives better results!

need R_0^{AB} , ε^{AB}

often obtained from atomic softness parameters:

$$R_0^{AB} = R_0^A + R_0^B$$

$$\varepsilon^{AB} = \sqrt{\varepsilon^A \varepsilon^B}$$

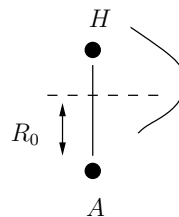
more complicated rules available

[*T. A. Halgren, J. Am. Chem. Soc.* **114**, 7827 (1992)]

in the above treatment atoms are assumed to be spherical

\rightarrow particularly bad approximation for hydrogen (with only one e^- that is displaced toward the other atom)

\Rightarrow smaller radius, depending on neighboring atom



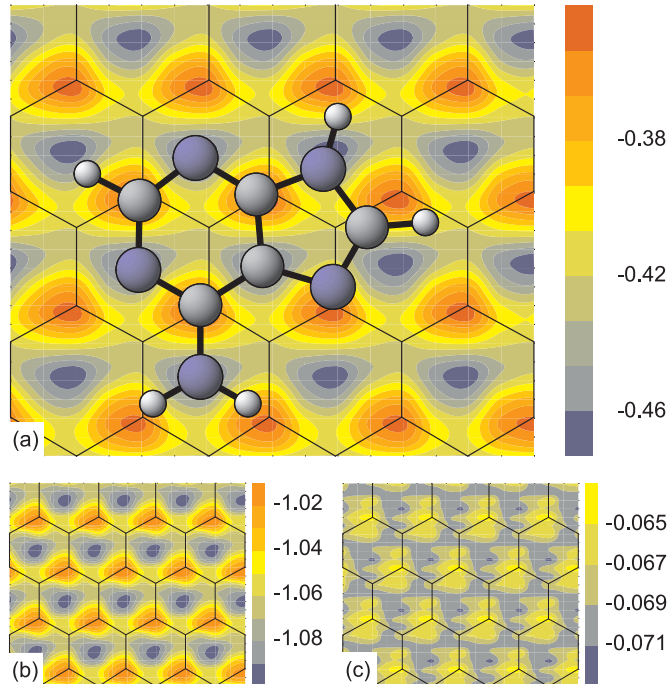
Similar, force field inspired approaches are recently frequently used to supplement density functional (DFT) calculations that do not account for dispersion forces by an additional van der Waals term. One approach, proposed in *W.G. Schmidt et al. Phys. Rev. Lett.* **95**, 186101 (2005) is based on the London dispersion formula

$$E_{ij}^{vdW}(r) = -\frac{3}{2r^6} \frac{\alpha_i \alpha_j I_i I_j}{I_i + I_j}. \quad (1)$$

and approximates the vdW interaction within pairs of atomic constituents i, j from their respective polarizabilities α and ionization energies I for large atomic distances r . In order to avoid the r^{-6} singularity, and because the short-range correlations are already contained in DFT, a cutoff function quenches the interaction for distances below the sum of the covalent radii r_{ij} of atoms i and j

$$f(r) = 1 - \exp \left[-\lambda \left(\frac{r}{r_{ij}} \right)^8 \right]. \quad (2)$$

The parameter λ are obtained from the requirement that $f(r)E_{ij}^{vdW}(r)$ leads to the correct graphite c lattice constant. Approaches like this are termed DFT-D. Shown below is the PES for adenine adsorbed on graphene calculated with DFT-LDA (a), DFT-D (b), and DFT-GGA (c). Energies are given in eV.



Hydrogen bonds: modified LJ

$$E_{H-bond}(R) = \varepsilon \left[5 \left(\frac{R_0}{R} \right)^{12} - 6 \left(\frac{R_0}{R} \right)^{10} \right]$$

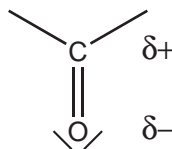
or considered within electrostatic energy

$$\begin{aligned} E(\text{cov. single bond}) &\approx 60 \dots 110 \text{ kcal/mol (2.6... 4.8 eV)} \\ E(\text{H - bond}) &\approx 2 \dots 5 \text{ kcal/mol (0.1... 0.2 eV)} \\ E(\text{vdW}) &\approx 0.1 \dots 0.2 \text{ kcal/mol (0.004... 0.01 eV)} \end{aligned}$$

Electrostatic Energy

Example: Carbonyl group

internal distribution of electrons creates positive and negative parts of the molecule



→ may be modelled by assigning **point charges** to each atom

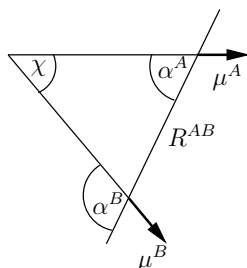
$$E_{el}(R^{AB}) = \frac{Q^A Q^B}{\varepsilon R^{AB}}$$

ε : dielectric constant

Q^A, Q^B usually obtained by fitting the electrostatic potential to the one obtained by an ab initio method

alternative: dipole description (e.g. in MM2, MM3)

assign dipoles to each bond



$$E_{el}(R^{AB}) = \frac{\mu^A \mu^B}{\varepsilon (R^{AB})^3} (\cos \chi - 3 \cos \alpha^A \cos \alpha^B)$$

ε : effective dielectric constant

typically $\varepsilon = 1 \dots 4$ (solvent molecules, screening within the molecule)

numerically efficient $\varepsilon \stackrel{!}{=} \varepsilon_0 \cdot R^{AB}$

$$\Rightarrow E_{el} \sim \frac{Q_A Q_B}{\varepsilon_0 (R^{AB})^2}$$

Remarks

- ▶ approximate screening (larger in larger molecules!)
- ▶ avoid square root (numerics!)

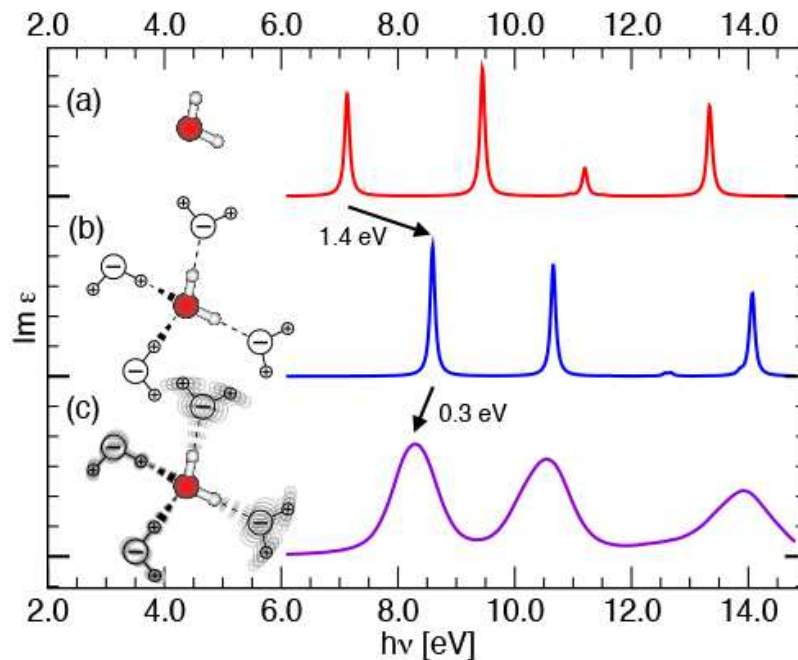
- ▶ no theoretical justification!

standard electrostatic term only contains two-body contributions, for polar species the **three-body contribution** is quite significant, about 10 – 20 % of the two-body term

three-body effect: interaction between two atomic charges being modified because a third atom polarizes the charges

Example: $\mu(\text{H}_2\text{O})^{\text{gas-phase}} = 1.8 D$
 $\mu(\text{H}_2\text{O})^{\text{ice}} = 2.5 D$

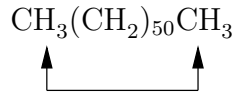
The polarization of single water molecules due to the neighbouring molecules also modifies its optical spectrum considerably. In fact, the optical response of ice and liquid water (and in particular its difference to gas phase molecules can nicely be understood from optical response calculations of single molecules embedded in the appropriate electrostatic environment. This is shown below. *From W.G. Schmidt et al. Phys. Rev. Lett. 100, 207403 (2008).*



The neglect of polarization is probably one of the main limitations of modern force fields!

How far apart should atoms be, in order to consider bonded/non-bonded energy terms?

Example:



obviously only non-bonded terms such as vdW, electrostatics

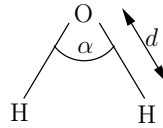
modern force fields:

| | |
|--------------|-------------------|
| E_{str} | 1, 2 pairs |
| E_{bend} | 1, 3 pairs |
| E_{tors} | 1, 4 pairs |
| $E_{vdW,el}$ | $\geq 1, 4$ pairs |

Cross terms

Example: H₂O

Equilibrium:
 $\alpha = 104, 5^\circ$,
 $d = 0, 958 \text{ \AA}$



compress angle $\alpha \rightarrow \alpha = 90^\circ \Rightarrow d = 0, 968 \text{ \AA}$
 d stretched due to repulsion between H atoms

\Rightarrow introduce terms which depend both on length and angle

$$E_{str/bend} = k^{ABC} (\Theta^{ABC} - \Theta_0^{ABC}) ((R^{AB} - R_0^{AB}) + (R^{BC} - R_0^{BC}))$$

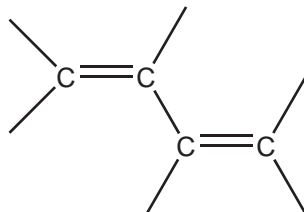
$$E_{str/str} = k^{ABC} (R^{AB} - R_0^{AB}) (R^{BC} - R_0^{BC})$$

$$E_{bend/bend} = k^{ABCD} (\Theta^{ABC} - \Theta_0^{ABC}) (\Theta^{BCD} - \Theta_0^{BCD})$$

... and so on!

Conjugated systems need special treatment

consider



all carbons of type 2 in MM2

⇒ same set of parameters to be used

⇒ obviously too simple!

⇒ perform simple electronic structure calculation (Pariser-Pople-Parr (PPP)-type, similar to extended Hückel theory (EHT) to be discussed later)

⇒ determine π -bond order ρ

$$\rho_{AB} = \sum_i^{MO} n_i C_{A_i} C_{B_i}$$

n_i : occupation

C_{B_i} : respective π -bonding orbital

⇒ measures π -contribution to bond

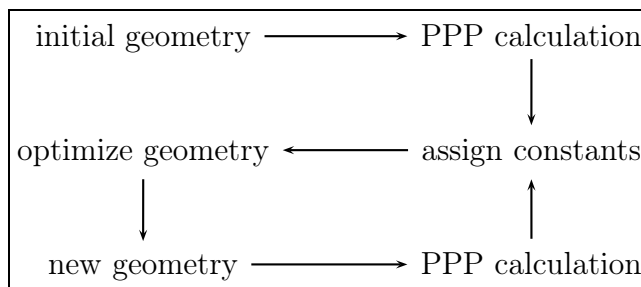
⇒ correct R_0, k :

$$R_0^{AB} = 1,503 - 0,166 \rho_{AB}$$

$$k^{AB} = 5,0 + 4,6 \rho_{AB}$$

practical implementation?

→ two-level optimization in MM2



2.2. Parameterization

Example: MM2 → 71 atom types

out of these 71 about 30 can form bonds with each other

- ▶ 71 atom types → 142 vdW parameters R_0^A, ε^A
- ▶ $30 \cdot 30/2 = 450 E_{str}$ terms
→ 900 parameters R_0^{AB}, k^{AB}
- ▶ $30 \cdot 30 \cdot 30/2 = 13500 E_{bend}$ terms
→ $\geq 27000 \Theta_0^{ABC}, k^{ABC}$
- ▶ $30 \cdot 30 \cdot 30 \cdot 30/2 = 405000 E_{tors}$ terms
→ $\geq 1215000 \begin{matrix} V_1^{ABCD} \\ V_2^{ABCD} \\ V_3^{ABCD} \end{matrix}$
- ▶ + cross terms

to assign the value of one parameter at least 3...4 independent data should be available

⇒ need about 10^7 exp. data

⇒ clearly impossible! in particular torsional constants are difficult to determine experimentally

⇒ take experiment mainly for vdW (difficult to describe in electronic structure theory)

& fit rest of parameters mainly to results of ab initio electronic structure calculations

still, cannot describe all theoretically possible compounds, parameters available in

| | | | |
|------|------------|------|---------------------------|
| MM2: | E_{vdW} | 142 | |
| | E_{str} | 290 | ~ 0.2% of possible amount |
| | E_{bend} | 824 | |
| | E_{tors} | 2466 | |

→ however, about 20% of the 15 million known compounds can be modelled

Experimental values have different accuracy depending on specific method

→ need weights

→ minimize merit function $\sum_{data_i} weight_i x_i$
 $x_i = (reference\ value_i - calculated\ value_i)^2$

→ try to find global minimum, difficult;
 see Norby and Liljefors, *J. Comput. Chem.* **19**, 1146 (1997)

⇒ Parameters are just that, parameters! Parameters are not transferable between different force fields.

New development: Universal Force Field (UFF)

see *A. K. Rappe et al. J. Am. Chem. Soc.* **114**, 10024 (1992)

derive di-, tri- and tetra-atomic parameters $E_{str.}$, E_{bend} , E_{tors} from atomic constants such as atomic radii, ionization potentials, electronegativities, polarizabilities etc.

physicist's comment: if done well, this should lead to empirical pseudopotentials!?

2.3. Computational

Non-bonded energy is by far the most time-consuming

Example: $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$

| n | N_{at} | Number of terms for calculating | | | |
|-----|----------|---------------------------------|------------|------------|-------------------------------|
| | | $E_{str.}$ | E_{bend} | E_{tors} | E_{vdW} |
| 10 | 32 | 31 | 30 | 81 | 405 |
| 100 | 302 | 301 | 600 | 891 | 44550 |
| | N | $N - 1$ | $2(N - 2)$ | $3(N - 5)$ | $\frac{N(N - 1)}{2} - 3N + 5$ |

⇒ In the limit of large molecules the computational time for calculating the force field energy grows as the square of the number of atoms

⇒ introduce cutoff radius for vdW $\sim 10 \dots 20 \text{ \AA}$

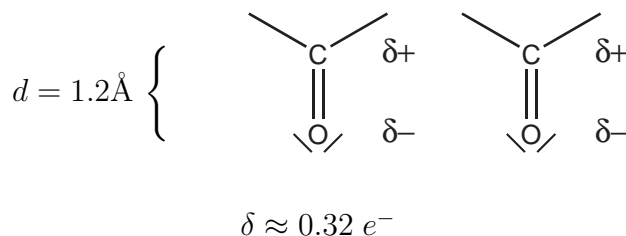
problem: all distance must be calculated prior to the decision of whether to include the contribution

- ⇒ set up list of non-bounded atoms which is regularly updated
 ⇒ $O(N)$ scaling in theory, actual calculations scale $O(N^{1.5...1.8})$, because theoretical limit only reached for very large molecules

Coulomb interaction $\sim R^{-1}$ ⇒ no cutoff radius possible

However, this is true only for molecules with a net charge (occurs very rarely), otherwise we have dipole-dipole in the actions $\sim R^{-3}$

Example: two carbonyl groups



| $R/\text{\AA}$ | E_{vdW}/eV | $E_{dipole-dipole}/eV$ | $E_{\delta-\delta}/eV$ net charges for comparison |
|------------------|--------------------|------------------------|---|
| 5 | $9 \cdot 10^{-3}$ | $1.7 \cdot 10^{-2}$ | 0.3 |
| 20 | $1 \cdot 10^{-6}$ | $2.7 \cdot 10^{-4}$ | 0.07 |
| 100 | $6 \cdot 10^{-11}$ | $2.1 \cdot 10^{-6}$ | 0.01 |
| $1.5 \cdot 10^6$ | - | - | $1 \cdot 10^{-6}$ |

cutoff radius of 10^6 \AA clearly too large to be of practical value

→ use either **Ewald method**

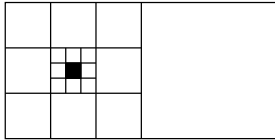
($\sim O(N^{\frac{3}{2}})$, periodic boundary conditions,
P. P. Ewald, Ann. Physik 64, 253 (1921))

or

Fast Multipole Moment (FMM) Method:

[*J. M. Perez - Jorda and W. Yang, Chem. Phys. Lett. 282, 71 (1998)*]

idea: split the contributions to E_{el} into near- and far-field
 → calculate near-field exactly
 → approximate far-field by multipoles situated at the centres of boxes



scaling $\sim O(N)$,
 large prefactor
 \Rightarrow cross-over with Ewald for about
 100000 particles

Typical accuracy of force fields?

Example: MM2

| compound type | average error in $\Delta H_f/eV$ |
|--------------------|----------------------------------|
| Hydrocarbons | 0.02 |
| Carbonyl compounds | 0.03 |
| Aromatic amines | 0.13 |

average error in exp. data: 0.02 eV

\Rightarrow MM2 reproduces hydrocarbons about as accurate as the experiment!

Examples for popular force fields:

functional forms for energy

(torsional energy is always Fourier series in the torsional angle)

| Force Field | Types | E_{str} | E_{bend} | E_{oop} | E_{vdw} | E_{el} | E_{cross} | Molecules |
|-------------|-------|------------------|-------------------|------------------|-------------------|---------------------|---------------------------|---|
| EAS | 2 | P2 | P3 | none | Exp.-6 | none | none | alkanes |
| EFF | 2 | P4 | P3 | none | Exp.-6 | none | ss,bb,sb, st,btb | alkanes |
| MM2 | 71 | P3 | P2+6 | P2 | Exp.-6 | dipole | sb | general |
| MM3 | 153 | P4 | P6 | P2 | Exp.-6 | dipole or charge | sb,bb,st | general (all elements) |
| MM4 | 3 | P6 | P6 | imp. | Exp.-6 | charge | ss,bb,sb, tt,st,tb,btb | hydrocarbons |
| CVFF | 53 | P2 or Morse | P2 | P2 | 6-12 | charge | ss,bb,sb, btb | general |
| CFE | 48 | P4 | P4 | P2 | 6-9 | charge | ss,bb,sb, sb,bt,btb | general |
| 91/93/95 | | | | | | | | |
| TRIPOS | 31 | P2 | P2 | P2 | 6-12 | charge | none | general |
| MMFF | 99 | P4 | P3 | P2 | 7-14 | charge | sb | general |
| COSMIC | 25 | P2 | P2 | P2 | Morse | charge | none | general |
| DREIDING | 37 | P2 or Morse | P2(cos) | P2(cos) | 6-12 or Exp.-6 | charge | none | general |
| AMBER | 41 | P2 | P2 | imp. | 6-12 10-12 | charge | none | proteins, nucleic acids carbohydrates |
| OPLS | 41 | P2 | P2 | imp. | 6-12 | charge | none | proteins nucleic acids carbohydrates |
| CHARMM | 29 | P2 | P2 | imp. | 6-12 | charge | none | proteins |
| GROMOS | | P2 | P2 | P2(imp.) | 6-12 | charge | none | proteins nucleic acids carbohydrates |
| ECEPP | | fixed | fixed | fixed | 6-12 10-12 | charge | none | proteins |
| MOMECC | | P2 | P2 | P2 | Exp.-6 | none | none | metal coordination |
| SHAPES | | P2 | $\cos(n\theta)$ | imp. | 6-12 | charge | none | metal coordination |
| ESFF | 97 | Morse | P2(cos) | P2 | 6-9 | charge | none | all elements |
| UFF | 126 | P2 or Morse | $\cos(n\theta)$ | imp. | 6-12 | charge | none | all elements |

Notation: P_n : Polynomial of order n ; $P_n(\cos)$: polynomial of order n in cosine to the angle; $\cos(n\theta)$: Fourier term(s) in cosine to the angle; Exp.-6: exponential $+R^{-6}$; n-m: $R^{-n} + R^{-m}$; fixed: not a variable; imp.: improper torsional angle; ss: stretch–stretch; bb: bend–bend; sb: stretch–bend; st: stretch–torsional; bt: bend–torsional; tt: torsional–torsional; btb: bend–torsional–bend.

3. The electronic problem

3.1. The Antisymmetry or Pauli Exclusion Principle

Electronic Hamiltonian introduced in 1 depends only on the spatial coordinates of the electrons. To completely describe an electron, however, we need to specify its **spin**.

→ introduce two spin functions $\alpha(w)$ & $\beta(w)$, corresponding to spin up and down, functions of an unspecified spin variable w , require that

$$\int dw \alpha^*(w) \alpha(w) = \int dw \beta^*(w) \beta(w) = 1 \quad (3)$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \quad (4)$$

and

$$\int dw \alpha^*(w) \beta(w) = \int dw \beta^*(w) \alpha(w) = 0 \quad (5)$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \quad (6)$$

→ altogether four coordinates for one electron, three spatial coordinates r , one spin coordinate w

→ $x = \{r, w\}$

→ wave function of an N -electron system is then a function of x_1, x_2, \dots, x_N , we write

$$\Phi(x_1, x_2, \dots, x_N)$$

Because Hamiltonian makes no reference to spin (at least by now), simply making the wave function dependent on spin does not lead anywhere

⇒ make an additional requirement on a wave function

A many-electron wave function must be antisymmetric with respect to the interchange of the coordinates x (both spin and space) of any two electrons:

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_n) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_n)$$

”antisymmetry principle”, ”Pauli exclusion principle”

independent postulate of quantum mechanics, W. Pauli, 1925

Nomenclature:

- ▶ orbital: wave function for a single electron
- ▶ molecular orbital: wave function for a single electron in a molecule
- ▶ spatial orbital $\psi_i(r)$: function of the position vector r , describes the spatial distribution of an electron such, that $|\psi_i(r)|^2 dr$ is the probability of finding e^- in the volume element dr surrounding r
usually assumed to form orthonormal set

$$\int dr \psi_i^*(r) \psi_j(r) = \delta_{ij}$$

- ▶ spin orbital $\chi(x)$: wave function for an electron that describes both its spatial distribution and its spin

From each spatial orbital $\psi(r)$ one can form two different spin orbitals

$$\chi(x) = \begin{cases} \psi(r)\alpha(w) & (\uparrow) \\ \psi(r)\beta(w) & (\downarrow) \end{cases}$$

3.2. Hartree Products

attempt to describe many-electron wave function by a simple product of spin orbital wave functions for each electron

$$\Psi^{HP}(x_1, \dots, x_N) = \chi_i(x_1)\chi_j(x_2) \dots \chi_k(x_N)$$

The Hartree product is an uncorrelated or independent-electron wave function because

$$\begin{aligned} & |\Psi^{HP}(x_1 \dots x_N)|^2 dx_1 \dots dx_N \\ &= |\chi_i(x_1)|^2 dx_1 |\chi_j(x_2)|^2 dx_2 \dots |\chi_k(x_N)|^2 dx_N \end{aligned}$$

i.e. the simultaneous probability of finding electron 1 in the volume element dx_1 and at the same time electron 2 in dx_2 , etc. is just equal the product of probabilities that electron 1 is in dx_1 times the probability that electron 2 is in dx_2 etc.

Search now for spin orbitals $\chi_i(x_k)$ for a given Hamiltonian, i.e.

$$H^e = \sum_{k=1}^N -\frac{1}{2} \nabla_k^2 + \sum_{k=1}^N v(r_k) + \frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{1}{|r_k - r_{k'}|} \quad (7)$$

$$\begin{array}{c} \downarrow \\ \text{external potential} \\ \text{(molecule constituents)} \end{array} \quad (8)$$

H^e contains no spin-orbit or spin-spin coupling
 \Rightarrow product ansatz for spin functions exact

\rightarrow consider in the following only the spatial orbitals
 $\psi^{HP}(r_1 \dots r_N) = \psi_1(r_1) \psi_2(r_2) \dots \psi_N(r_N)$

employ variational principle

$$E^e \leq \langle \psi^{HP} | H^e | \psi^{HP} \rangle$$

$$\begin{aligned} \langle \psi^{HP} | H^e | \psi^{HP} \rangle &= E_{Hartree}[\psi^{HP}] \\ &= \sum_k \int \dots \int \psi_1^*(r_1) \dots \psi_N^*(r_N) \left\{ -\frac{1}{2} \nabla_k^2 + v(r_k) \right\} \\ &\quad \times \psi_1(r_1) \dots \psi_N(r_N) dr_1 \dots dr_N \\ &\quad + \int \dots \int \psi_1^*(r_1) \dots \psi_N^*(r_N) \left\{ \frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{1}{|r_k - r_{k'}|} \right\} \\ &\quad \times \psi_1(r_1) \dots \psi_N(r_N) dr_1 \dots dr_N \\ &= \sum_{k=1}^N \int \psi_k^*(r) \left\{ -\frac{1}{2} \nabla_k^2 + v(r_k) \right\} \psi_k(r) dr \\ &\quad + \sum_{k,k'}^{N,N} \frac{1}{2} \int \int \psi_k^*(r) \psi_{k'}^*(r') \frac{1}{|r - r'|} \psi_k(r) \psi_{k'}(r') dr dr' \end{aligned} \quad (9)$$

vary $E_{Hartree}$ with respect to $\psi_i^*(r)$ or $\psi_j(x)$, respectively, variation not completely free, since we are restricted to functions that can be normalized to 1

\rightarrow Lagrange multipliers

\rightarrow search for minimum of

$$E_{Hartree}[\psi^{HP}] - \sum_k \varepsilon_k \langle \psi_k | \psi_k \rangle \quad (10)$$

i.e.

$$\delta \left\{ E_{Hartree}[\psi_1, \dots, \psi_N] - \sum_k \varepsilon_k \langle \psi_k | \psi_k \rangle \right\} = 0 \quad (11)$$

i.e.

$$\begin{aligned} & \langle \delta\psi_i \left| -\frac{\nabla_k^2}{2} + v(r) \right| \psi_i \rangle + \sum_{k \neq i} \langle \delta\psi_i(r) \psi_k(r') \left| \frac{1}{|r-r'|} \right| \psi_i(r) \psi_k(r') \rangle \\ & \quad - \varepsilon_i \langle \delta\psi_i | \psi_i \rangle = 0 \\ \Rightarrow & \left[-\frac{\nabla}{2} + v(r) \right] \psi_i(r) + \sum_{k \neq i} \langle \psi_k(r') \left| \frac{1}{|r-r'|} \right| \psi_k(r') \rangle \\ & \quad \times \psi_i(r) = \varepsilon_i \psi_i(r) \\ \Rightarrow & \boxed{\left[-\frac{\nabla^2}{2} + v(r) \right] \psi_i(r) + \left[\int \frac{n(r')}{|r-r'|} dr' - \int \frac{|\psi_i(r')|^2}{|r-r'|} dr' \right] \psi_i(r) = \varepsilon_i \psi_i} \\ & \quad \text{Hartree equation} \end{aligned} \quad (12)$$

where $n(r) = \sum_k |\psi_k(r)|^2$

the third term in the above equation is the electrostatic potential due to the electrons, it is called "Hartree potential"

$$V_{Hartree}(r) = \int \frac{n(r')}{|r-r'|} dr' \quad (13)$$

the last term in the square brackets is the correction to the Hartree potential, an electron in orbital $\psi_i(r)$ should not interact with itself, but only with the other $N-1$ electrons

→ self-interaction correction "SIC"

The Hartree equation can be formally written as a single-particle equation

$$\left\{ -\frac{\nabla^2}{2} + V_{eff}(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r) \quad (14)$$

however the "effective potential" depends itself on the solutions $\psi_i(r)$

$$V_{eff}(r) = v(r) + V_{Hartree}(r) - v_{SI} \quad (15)$$

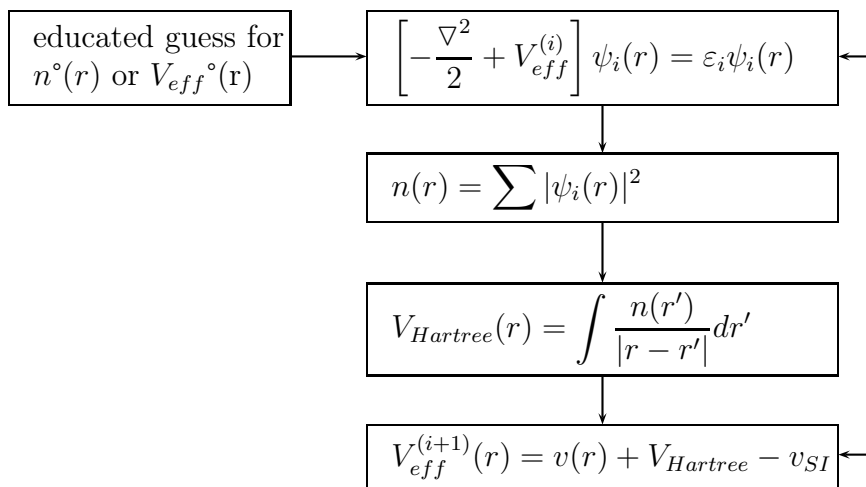
with

$$v(r) = - \int \frac{n^+(r')}{|r - r'|} dr' \leftarrow \text{nuclei} \quad (16)$$

$$V_{Hartree} = \int \frac{n(r)}{|r - r'|} dr' \quad (17)$$

$$v_{SI} = \text{self-interaction} \quad (18)$$

Therefore the Hartree equations are solved using a self-consistent field method



until self-consistency is reached.

a good approximation for the first charge density of the molecule is given by the superpositions of atomic charge densities

$$n^\circ(r) = \sum_i n_i^{Atom}(r - R_i)$$

(which is correct for large interatomic distances)

There is a basic deficiency in the Hartree product, it takes no account of the indistinguishability of electrons. The antisymmetry principle that holds for indistinguishable fermions requires that the electronic wave functions is antisymmetric (changes sign) with respect to the interchange of the space and spin coordinates of any two electrons

⇒ There is no many-electron system that is correctly described with the Hartree equations!

(However, charge density often not bad)

3.3. Hartree-Fock Approximation

major problem with Hartree products:
violate Pauli principle

⇒ use antisymmetrizing operator A

$$\Psi^{HF}(x_1, \dots, x_N) = A[\chi_1(x_1)\chi_2(x_2) \dots \chi_N(x_N)]$$

such that

$$\Psi^{HF}(x_1, \dots, x_i, \dots, x_k, \dots, x_N) = -\Psi^{HF}(x_1, \dots, x_k, \dots, x_i, \dots, x_N)$$

This requirement can be fulfilled by taking a linear combination of Hartree products that are written as a determinant. For an N-electron system, the Slater determinant is defined as

$$\Psi^{HF}(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \dots & \chi_N(x_1) \\ \vdots & & \vdots \\ \chi_1(x_N) & \dots & \chi_N(x_N) \end{vmatrix}.$$

By definition this wave function is consistent with the Pauli principle

Example: 2 electron system

$$\Psi^{HF} = \frac{1}{\sqrt{2}} \{ \chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1) \}$$

χ_i orthogonal, normalized

$$\langle \Psi^{HF} | \Psi^{HF} \rangle \tag{19}$$

$$\begin{aligned} &= \frac{1}{2} \int dx_1 dx_2 \{ \chi_1^*(x_1)\chi_2^*(x_2)\chi_1(x_1)\chi_2(x_2) \\ &\quad - \chi_1^*(x_1)\chi_2^*(x_2)\chi_1(x_2)\chi_2(x_1) \\ &\quad - \chi_1^*(x_2)\chi_2^*(x_1)\chi_1(x_1)\chi_2(x_2) \\ &\quad + \chi_1^*(x_2)\chi_2^*(x_1)\chi_1(x_2)\chi_2(x_1) \} \\ &= \frac{1}{2} \{ 1 - 0 - 0 + 1 \} = 1 \end{aligned} \tag{20}$$

proceed now in analogy to Hartree products, calculate

$$E^{HF} = \langle \Psi^{HF} | H^e | \Psi^{HF} \rangle \geq E_e$$

$$\begin{aligned}
E^{HF}[\psi^{HF}] &= \sum_{i=1}^N \int dx_1 \chi_i^*(x_i) \left\{ -\frac{\nabla^2}{2} + v(r_i) \right\} \chi_i(x_i) \\
&+ \frac{1}{2} \sum_{i \neq j}^{N,N} \int \int dx_i dx_j \frac{\chi_i^*(x_i) \chi_j^*(x_j) \chi_i(x_i) \chi_j(x_j)}{|r_i - r_j|} \\
&- \frac{1}{2} \sum_{i \neq j}^{N,N} \int \int dx_i dx_j \frac{\chi_j^*(x_i) \chi_i^*(x_j) \chi_i(x_i) \chi_j(x_j)}{|r_i - r_j|}
\end{aligned}$$

integration over spin variable

$$\chi_i(x) = \psi_i(r) \eta_i(w)$$

$$\int dw \eta_i(w)^* \eta_j(w) = \delta_{s_i s_j}$$

→ in first line above: $\int dw_i \eta_i^*(w_i) \eta(w_i) = 1$

→ in second line:

$$\begin{aligned}
&\int \int dw_i dw_j \eta_i^*(w_i) \eta_j^*(w_j) \eta_i(w_i) \eta_j(w_j) & (21) \\
&= \int dw_i \eta_i^*(w_i) \eta_i(w_i) \int dw_j \eta_j^*(w_j) \eta_j(w_j) = 1
\end{aligned}$$

→ in third line:

$$\begin{aligned}
&\int \int dw_i dw_j \eta_j^*(w_i) \eta_i^*(w_j) \eta_i(w_i) \eta_j(w_j) & (22) \\
&= \int dw_j \eta_i^*(w_j) \eta_j(w_j) \int dw_i \eta_j^*(w_i) \eta_i(w_i) \\
&= \delta_{s_i s_j}
\end{aligned}$$

⇒ go over to spatial orbitals

$$\begin{aligned}
 E^{HF} [\psi^{HF}] &= \sum_{k=1}^N \int d^3r \psi_k^*(r) \left\{ -\frac{\nabla^2}{2} + v(r) \right\} \psi_k(r) \\
 &+ \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{1}{2} \int \int d^3r d^3r' \psi_k^*(r) \psi_{k'}^*(r') \frac{1}{|r-r'|} \psi_k(r) \psi_{k'}(r') \\
 &- \underbrace{\sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \delta_{s_k s_{k'}} \frac{1}{2} \int \int d^3r d^3r' \psi_k^*(r') \psi_{k'}^*(r) \frac{1}{|r-r'|} \psi_k(r) \psi_{k'}(r')}_{\tilde{E}_x} \\
 &= E^{Hartree} + \tilde{E}_x
 \end{aligned} \tag{23}$$

i.e. compared to Hartree theory we have now an additional term, \tilde{E}_x

\tilde{E}_x : exchange term, due to exchange interaction enforced by complying with Pauli principle

$\tilde{E}_x < 0 \Rightarrow$ lowers energy compared to Hartree theory, i.e. HF is better approximation than Hartree

Can split E^{HF} according to

$$E^{HF} = T_S + E_{en} + E_H + E_x$$

where

$$T_S = \sum_{k=1}^N \int \psi_k^*(r) \left(-\frac{\nabla^2}{2} \right) \psi_k(r) d^3r \tag{24}$$

$$E_{en} = \int v(r) n(r) d^3r \tag{25}$$

$$E_H = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' \tag{26}$$

$$E_x = -\frac{1}{2} \sum_{k,k'}^{N,N} \delta_{s_k s_{k'}} \int \int d^3r d^3r' \frac{\psi_k^*(r') \psi_{k'}^*(r) \psi_{k'}(r') \psi_k(r)}{|r-r'|} \tag{27}$$

with $n(r) = \sum_{k=1}^N |\psi_k(r)|^2$ and

$$E_x = \tilde{E}_x - E_{SI}$$

E_{SI} : self-interaction, term with $k = k'$ which is not excluded above, because it cancels with $k = k'$ term in E_H

Nowadays E_x is called exchange energy. Strictly speaking, however, E_x also contains correction of self-interaction.

The "best" functions $\psi_k(r)$ can be obtained by employing the variational principle. Again, we have to satisfy that the ψ_k can be normalized to one and are orthogonal

$$\Rightarrow \delta \left\{ \underbrace{E^{HF} - \sum_{i,j} \lambda_{i,j} \langle \psi_i | \psi_j \rangle}_{=Q[\psi_1, \dots, \psi_N]} \right\} = 0$$

$$\begin{aligned} & Q[\psi_1, \dots, \psi_k + \delta\psi_k, \dots, \psi_N] - Q[\psi_1, \dots, \psi_k, \dots, \psi_N] & (28) \\ &= \int \delta\psi_k^*(r) \left\{ -\frac{\nabla^2}{2} + v(r) \right\} \psi_k(r) d^3r \\ &+ \frac{1}{2} \int \int \frac{\delta\psi_k^*(r) n(r') \psi_k(r)}{|r - r'|} d^3r d^3r' \\ &- \frac{1}{2} \sum_{i=1}^N \delta_{s_i s_k} \int \int \frac{\delta\psi_k^*(r) \psi_i^*(r') \psi_i(r) \psi_k(r')}{|r - r'|} d^3r d^3r' \cdot 2 \\ &- \sum_i^N \lambda_{ik} \int \delta\psi_k^*(r) \psi_i(r) d^3r = 0 \end{aligned}$$

valid for any variation $\delta\psi_k$

$$\begin{aligned} \Rightarrow \quad & \left\{ -\frac{\nabla^2}{2} + v(r) + \int \frac{n(r')}{|r - r'|} d^3r' \right\} \psi_k(r) \dots & (29) \\ & - \sum_j \delta_{s_j s_k} \int \frac{\psi_j^*(r') \psi_k(r') \psi_j(r)}{|r - r'|} d^3r' = \sum_i \lambda_{ik} \psi_i(r) \\ & \quad \downarrow \\ & \text{index renamed } i \rightarrow j \end{aligned}$$

apply $\int d^3r \psi_i^*(r)$

$$\Rightarrow \lambda_{ik} = \underbrace{\int \psi_i^*(r) \{ \dots \} \psi_k(r) d^3r}_{A_{ik}=(A_{ki})^*} \dots \quad (30)$$

$$- \underbrace{\sum_j \delta_{s_j s_k} \int \int \frac{\psi_i^*(r) \psi_j^*(r') \psi_k(r') \psi_j(r)}{|r - r'|} d^3r d^3r'}_{B_{ik}=(B_{ki})^*}$$

$\Rightarrow \lambda_{ik}$ hermitian, \exists unitary transformation so that

$$\lambda_{ik} \rightarrow \varepsilon_k \delta_{ik}$$

$$\psi_k \rightarrow \tilde{\psi}_k$$

$$\Rightarrow \boxed{\begin{array}{l} HF \text{ Equation} \\ \left\{ -\frac{\nabla^2}{2} + v(r) + V_{Hartree}(r) + V_x^{(k)}(r) \right\} \tilde{\psi}_k(r) = \varepsilon_k \tilde{\psi}_k(r) \\ \text{with } V_x^{(k)}(r) \tilde{\psi}_k(r) = - \sum_{i=1}^N \delta_{s_i s_k} \int \frac{\tilde{\psi}_i^*(r') \tilde{\psi}_k(r') \tilde{\psi}_i(r)}{|r - r'|} d^3r' \end{array}}$$

exchange term is not a normal potential, but an integral operator

multiply with $\frac{\tilde{\psi}_k(r)}{\tilde{\psi}_k(r)}$

and define $n_k^{HF}(r, r') = \sum_{i=1}^N \delta_{s_i s_k} \frac{\tilde{\psi}_i^*(r') \tilde{\psi}_k(r') \tilde{\psi}_i(r)}{\tilde{\psi}_k(r)}$ as exchange density, then we obtain for the exchange potential

$$V_x^{(k)}(r) = - \int \frac{n_k^{HF}(r, r')}{|r - r'|} d^3r'$$

The potential is particle specific, describes interaction of particle k with the other electrons. However, only interactions with particles with the same spin, i.e. $s_i = s_k$

Remark

in the following we don't write the $\tilde{}$ anymore

What is the meaning of the Lagrange parameters ε_k ?

Energy required to remove electron from state k in a N -electron system given by

$$I_k = \langle \Psi^{N-1} | H^{e, N-1} | \Psi^{N-1} \rangle \quad (31)$$

$$- \langle \Psi^N | H^{e, N} | \Psi^N \rangle$$

3 The electronic problem

Ψ^N : ground state of N -electron system
 Ψ^{N-1} : ground state of $N - 1$ -electron system
 $k = \text{HOMO} \iff I_k$: ionization energy

two approximations:

- (i) vertical ionization \iff no molecular relaxation
 - (ii) removal of k -th electron does not change the single-particle wave functions of the remaining electrons (only extended states and localized perturbations well described within this approximation)
- (i) & (ii) $\Rightarrow \Psi^{N-1}$ can be obtained from Ψ^N by removal of k -th column and k -th row from the Slater determinant

$$\begin{aligned}
 \Rightarrow I_k &= \sum_{\substack{i=1 \\ i \neq k}}^{N,N} \langle \psi_i \left| -\frac{\nabla^2}{2} + v(r) \right| \psi_i \rangle & (32) \\
 &+ \frac{1}{2} \sum_{\substack{i,j \\ i \neq j, i \neq k \\ j \neq k}}^{N,N} \int \int d^3r d^3r' \frac{\psi_i^*(r) \psi_j^*(r') \psi_i(r) \psi_j(r')}{|r - r'|} \\
 &- \frac{1}{2} \sum_{\substack{i,j \\ i \neq j, i \neq k \\ j \neq k}}^{N,N} \delta_{s_i s_j} \int \int d^3r d^3r' \frac{\psi_j^*(r) \psi_i^*(r') \psi_i(r) \psi_j(r')}{|r - r'|} \\
 &- \{ \text{above expression with } i = k, j = k \text{ included} \} \\
 &= - \langle \psi_k \left| -\frac{\nabla^2}{2} + v(r) \right| \psi_k \rangle \\
 &- \frac{1}{2} \sum_{\substack{i=1 \\ i \neq k}}^N 2 \int \int d^3r d^3r' \frac{\psi_i^*(r) \psi_k^*(r') \psi_i(r) \psi_k(r')}{|r - r'|} \\
 &+ \frac{1}{2} \sum_{\substack{i=1 \\ i \neq k}}^N 2 \delta_{s_i s_k} \int \int d^3r d^3r' \frac{\psi_k^*(r) \psi_i^*(r') \psi_i(r) \psi_k(r')}{|r - r'|} \\
 &= - \varepsilon_k
 \end{aligned}$$

\Rightarrow Lagrange parameters ε_k describe (approximately!) the energy required to remove one electron from orbital k
 Also excitation energies, i.e., transitions from occupied state i into unoccupied state j are (approximately) determined by the ε_k

$$\Delta E_{i \rightarrow j} \approx \varepsilon_j - \varepsilon_i$$

Koopman's theorem

[T. A. Koopmans, *Physica* **1**, 104 (1933)]

Remark

Eigenvalues corresponding to occupied orbitals are well defined and they converge to a specific value as the size of the basis set is increased. In contrast, unoccupied orbitals depend strongly on basis set used for the calculation

3.4. The exchange interaction

Effective one-body Hamiltonian for Hartree and HF:

$$-\frac{\nabla^2}{2} + v(r) - V_{Hartree} - \begin{cases} \int d^3r' \frac{n_k^H(r')}{|r-r'|} & \text{Hartree} \\ \int d^3r' \frac{n_k^{HF}(r, r')}{|r-r'|} & \text{HF} \end{cases}$$

where $n_k^H(r) = |\psi_k(r)|^2$

and $n_k^{HF}(r, r') = \sum_{i=1}^N \delta_{s_i s_k} \frac{\psi_i^*(r') \psi_k(r') \psi_i(r)}{\psi_k(r)}$

Obviously:

$$\int n_k^H(r) d^3r = 1 \quad (33)$$

$$\int n_k^{HF}(r, r') d^3r' = \sum_{i=1}^N \delta_{s_i, s_k} \delta_{ik} \frac{\psi_i(r)}{\psi_k(r)} = 1 \quad (34)$$

Both densities n_k^H and n_k^{HF} thus represent one electron, i.e., in both cases the self-interaction contained in $V_{Hartree}$ is corrected for.

However, n_k^{HF} , contains more!

Example: Jellium (actually not too bad a description for Na, Cs, Al etc.)

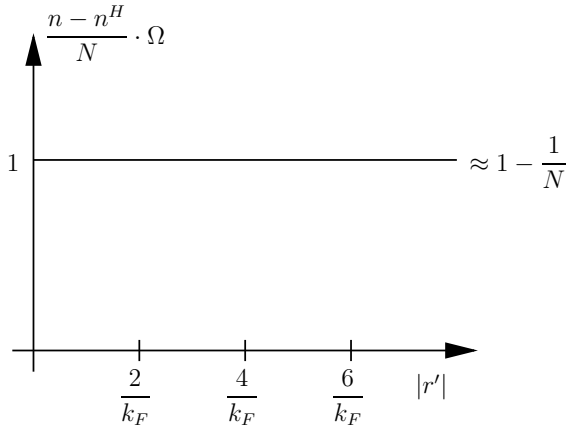
solution to Hartree and HF equations \rightarrow plane waves

$$\psi_i(r) = \frac{1}{\sqrt{\Omega}} e^{ik_i r} \quad (35)$$

$$\Rightarrow n_k^H(r) = \frac{1}{\Omega} = \text{const.} \quad (36)$$

That means the density of the k -th electron is uniformly distributed over the volume, the density acting on a Hartree electron is given by

$$n(r') - n_k^H(r') = \frac{N}{\Omega} - \frac{1}{\Omega}$$



distribution of $N - 1$ other electrons for particle k at $r = 0$ in Hartree approximation for jellium

consider now HF , $n(r') - n_k^{HF}(r, r')$?

$$n_k^{HF}(r, r') = \sum_i^N \delta_{s_i s_k} \frac{\psi_i^*(r') \psi_k(r') \psi_i(r)}{\psi_k(r)}$$

(if we assume each allowed state, i.e., k vector, to be occupied with spin-up and -down electron one has to replace $N \rightarrow N/2$)

$$= \frac{1}{\Omega} \sum_i^{N/2} e^{-ik_i r'} e^{ik_k r'} e^{ik_i r} e^{-ik_k r} \quad (37)$$

$$= \frac{1}{\Omega} e^{ik_k(r'-r)} \sum_i^{N/2} e^{ik_i(r-r')} \quad (38)$$

expression is still state dependent, for easier interpretation we average over all k

states

$$\bar{n}^{HF}(r, r') = \frac{1}{\underbrace{n(r)}_{\frac{N}{\Omega}}} \sum_k^N \underbrace{\psi_k^*(r)\psi_k(r)}_{\frac{1}{\Omega}} n_k^{HF}(r, r') \quad (39)$$

$$= \frac{\Omega}{N} \frac{1}{\Omega^2} \sum_k^{N/2} e^{ik_k(r-r')} \underbrace{\sum_i^{N/2} e^{ik_i(r-r')}}_S \quad (40)$$

$$\sum_i^{N/2} \rightarrow \frac{\Omega}{(2\pi)^3} \int_{k=0}^{k_F} d^3k, \quad \text{calculate } S$$

$$S = \frac{\Omega}{(2\pi)^3} \int_{k=0}^{k_F} d^3\bar{k} e^{i\bar{k}(\bar{r}-\bar{r}')} = S(\bar{r}'') \quad \bar{r}'' = (\bar{r} - \bar{r}')$$

$S(\bar{r}'') = S(|r''|)$ Why? Average over \bar{k} !

$$\Rightarrow S(r'') = \frac{\Omega}{(2\pi)^3} \int_0^{k_F} k^2 dk \cdot 2\pi \int_0^\pi d\theta \sin\theta e^{ikr'' \cos\theta} \quad (41)$$

$$= \frac{\Omega}{(2\pi)^3} \cdot \frac{4\pi}{r''^3} (k_F r'' \cos(k_F r'') - \sin(k_F r'')) \quad (42)$$

$$\frac{3N}{8\pi k_F^3} \leftarrow \text{Definition Fermi wave vector} \quad (43)$$

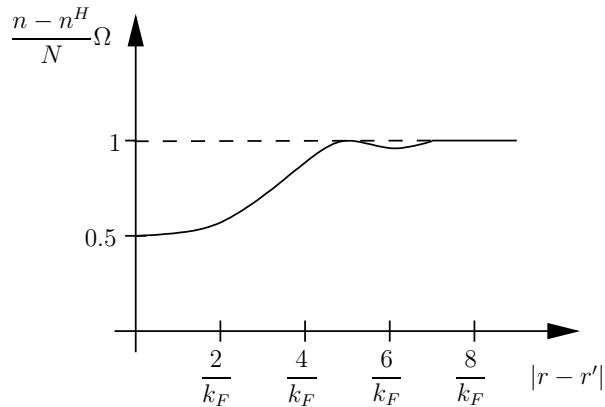
$$= \frac{3}{2} \frac{N}{(r'' k_F)^3} (k_F r'' \cos(k_F r'') - \sin(k_F r''))$$

analogous for first integral

$$\Rightarrow \boxed{\begin{aligned} \bar{n}^{HF}(r, r') &= \bar{n}^{HF}(|r''|) \\ &= \frac{9}{2} \frac{N}{\Omega} \left\{ \frac{1}{(k_F r'')^3} [k_F r'' \cos(k_F r'') - \sin(k_F r'')] \right\}^2 \end{aligned}}$$

Obviously, also the averaged n^{HF} is spherical

The concentration of electrons with the same spins is reduced in the vicinity of a given electron. The electron is surrounded by an "exchange hole". The Pauli principle leads to a correlation of electrons with the same spin. The quantity $n_k^{HF}(r - r')$ is the density of the "exchange hole" of an electron at r .



Difference between Hartree and HF: $n_k^H(r')$ depends only on r' , i.e. not on the coordinates of electron k . In contrast, $n_k^{HF}(r, r')$ depends on the position of the considered particle. n_k^{HF} accounts for Pauli principle: when electron k sits at r then all electrons with the same spin must be pushed away.

Another correlation between the particles should be due to the Coulomb repulsion between all the electrons, i.e., also between electrons of opposite spin. This Coulomb repulsion, however, is both in Hartree and HF only contained in an averaged manner, i.e., the respective correlation is missing.

The difference in energy between the HF and the lowest possible energy (in a given basis set) is called the **”Electron Correlation Energy”**. Physically it corresponds to the notion of correlated electrons being on average further apart than described by the HF wave function.

Consider eigenvalues of HF equations in jellium approximation

Hartree potential and external potential cancel each other because of

$$\text{charge neutrality: } v(r) + \int \frac{n(r')}{|r - r'|} d^3 r' = 0$$

$$\Rightarrow \varepsilon(k) = \frac{k^2}{2} + \langle \psi_k | V_x^{(k)} | \psi_k \rangle$$

$$\langle \psi_k | V_x^{(k)} | \psi_k \rangle = - \frac{1}{\Omega} \int d^3 r \int d^3 r' \frac{\psi_k^*(r) n_k^{HF}(r, r') \psi_k(r)}{|r - r'|} \quad (44)$$

plane wave
expansion

$$\stackrel{\downarrow}{=} \frac{1}{\Omega^2} \int d^3 r \int d^3 r' \frac{1}{|r - r'|} e^{ik(r'-r)} \int_0^{k_F} d^3 k' \frac{\Omega}{(2\pi)^3} e^{ik'(r-r')} \quad (45)$$

with Fourier expansion of Coulomb potential

$$\frac{1}{|r - r'|} = 4\pi \int \frac{d^3q}{(2\pi)^3} \frac{1}{q^2} e^{iq(r-r')}$$

it follows

$$\begin{aligned} \langle \psi_k | V_x^{(k)} | \psi_k \rangle &= \frac{1}{\Omega^2} \int d^3r \int d^3r' \int \frac{d^3q}{(2\pi)^3} \frac{1}{q^2} e^{iq(r-r')} \\ &\quad \times e^{ik(r'-r)} \int d^3k \frac{\Omega}{(2\pi)^3} e^{ik'(r-r')} \end{aligned} \quad (46)$$

to perform the r and r' integration we exploit

$$\int d^3r e^{-i(q-k+k')r} = (2\pi)^3 \delta(q - k + k')$$

$$\begin{aligned} \Rightarrow \langle \psi_k | V_x^{(k)} | \psi_k \rangle &= - \frac{4\pi}{(2\pi)^3} \int_0^{k_F} d^3k' \frac{1}{|k - k'|^2} \\ &= - \frac{1}{2\pi^2} \cdot 2\pi \int_0^{k_F} k'^2 dk' \int_0^\pi d\theta \sin \theta \frac{1}{k'^2 + k^2 - 2kk' \cos \theta} \\ &= - \frac{1}{\pi} \int_0^{k_F} k'^2 dk' \int_{-1}^1 d\eta \frac{1}{k'^2 + k^2 - 2kk'\eta} \\ &= - \frac{1}{\pi} \int_0^{k_F} dk' k' \frac{1}{k} \ln \left| \frac{k + k'}{k - k'} \right| \\ &= - \frac{1}{\pi} \left\{ \frac{k_F^2 - k^2}{2k} \ln \left| \frac{k_F + k}{k_F - k} \right| + k_F \right\} \\ &= - \frac{2}{\pi} k_F F \left(\frac{k}{k_F} \right) \end{aligned} \quad (47)$$

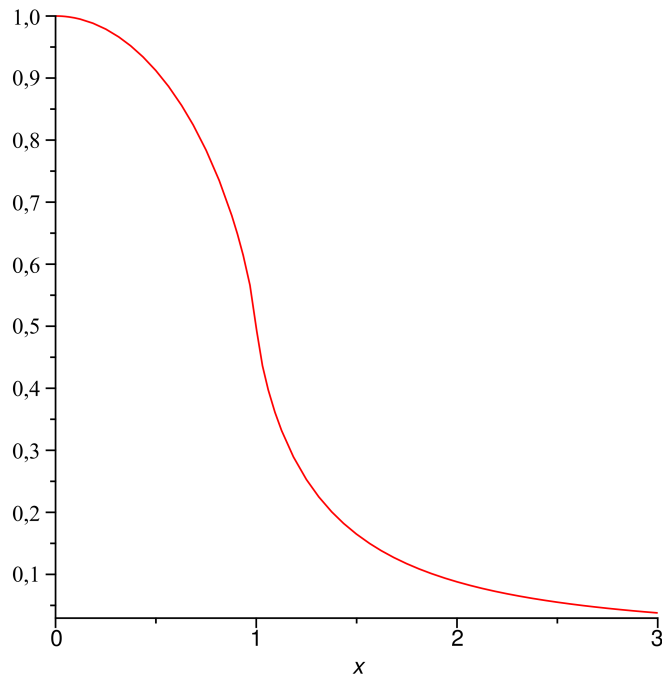
where $F(x) = \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| + \frac{1}{2}$

$$\Rightarrow \boxed{\varepsilon(k) = \frac{k^2}{2} - \frac{2}{\pi} k_F \cdot F \left(\frac{k}{k_F} \right)}$$

\Rightarrow plane waves are indeed eigenstates of HF Hamiltonian, but dispersion relation of free particles does not hold anymore

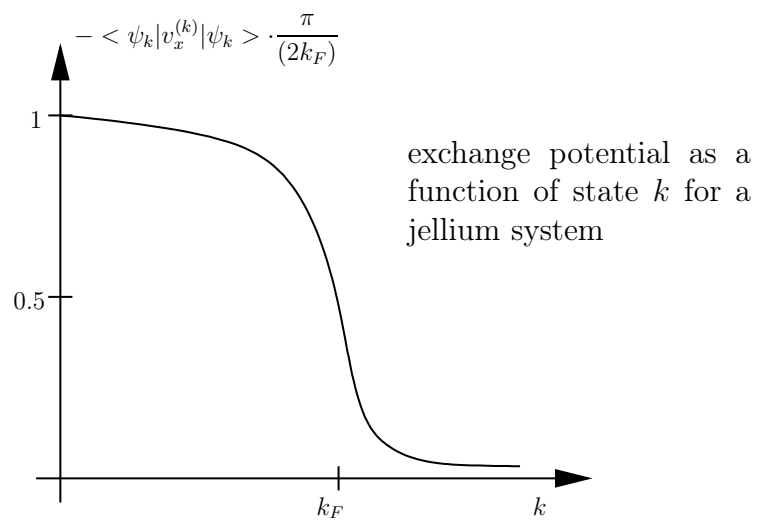
$f := x \rightarrow 0.5 + (1-x^2) * \ln(\text{abs}((1+x)/(1-x))) / (4*x); \text{plot}(f(x), x=0..3);$

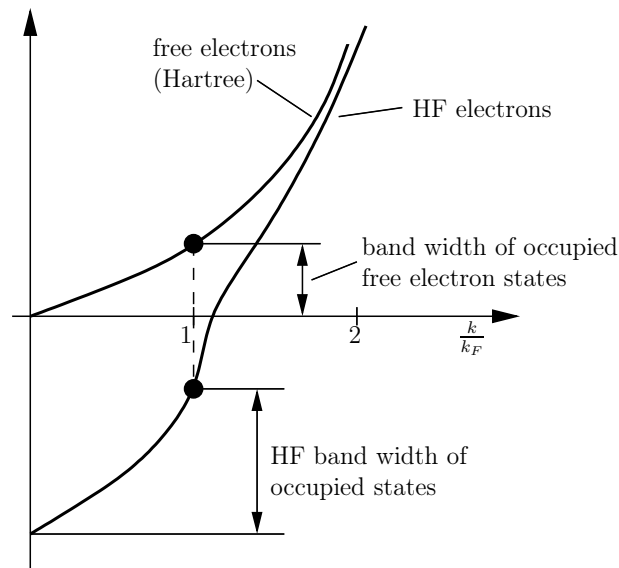
$$x \rightarrow 0.5 + \frac{1}{4} \frac{(1-x^2) \ln\left(\left|\frac{1+x}{1-x}\right|\right)}{x}$$



$\text{int}(4 * \text{Pi} * x * x * f(x) / (4 * \text{Pi} / 3), x=0..1);$

0.7500000000





$$\text{dispersion relation } \varepsilon^{HF}(k) = \frac{k^2}{2} - \frac{2}{\pi} k_F \cdot F\left(\frac{k}{k_F}\right)$$

Remark

- ▶ similar to the calculation of the expectation value above it can be shown that plane waves are eigenstates of the HF equations for jellium, this is not trivially clear as the exchange hole is non-local
- ▶ single-particle energies are lowered in HF compared to Hartree
- ▶ parabolic dispersion for $k \rightarrow 0$, but effective mass has changed

$$\frac{m^*}{m} = \frac{1}{1 + 0.22 \frac{r_s}{a_b}} \quad \text{for } k \rightarrow 0$$

(r_s ...Wigner-Seitz radius, defined by $\frac{4}{3}\pi r_s^3 = \frac{\Omega}{N}$)

- ▶ band width of occupied states is much enhanced
- ▶ The expression for $\varepsilon^{HF}(k)$ predicts that the derivative of the renormalized single-particle energy has a logarithmic divergence at $k = k_F$. Namely, on the Fermi surface the effective mass m^* and the density of single-particle states (proportional to m^*) vanish within Hartree-Fock. The main fault with the Hartree-Fock approximation is that by including exchange between electrons with parallel spins, but neglecting correlations due to the Coulomb repulsions which are most effective for electrons with antiparallel spins, it includes neither screening nor the collective plasma excitation.

3.5. Hartree-Fock-Slater theory (or X_α method)

The numerical inconvenience of HF results from the fact that the exchange potential is state dependent

for jellium we have obtained

$$V_x^{(k)} = -\frac{2}{\pi} k_F F\left(\frac{k}{k_F}\right)$$

using $k_F = \sqrt[3]{3\pi^2 n}$ we can express $V_x^{(k)}$ as function of the electron density;

to remove the state (i.e. k) dependence we can average $F\left(\frac{k}{k_F}\right)$ over all occupied states

$$\left(\frac{4}{3}\pi k_F^3\right)^{-1} \cdot \int_0^{k_F} 4\pi k^2 dk F\left(\frac{k}{k_F}\right) = 0.75$$

$$\Rightarrow \bar{F} = 0.75$$

One can also argue that only the electrons with $k = k_F$ i.e. at the Fermi edge are important for chemistry

$$\Rightarrow F \rightarrow F(1) = 0.5$$

$$\Rightarrow \bar{V}_x^{(k)} =: V_{x_\alpha} = \begin{cases} -\frac{3}{2\pi} \sqrt[3]{3\pi n} & \text{average over all occupied states of HF} \\ & \text{equation} \\ -\frac{1}{\pi} \sqrt[3]{3\pi n} & \text{consider only states at Fermi edge} \end{cases}$$

(i) HF is not exact anyway
(because correlation is missing)

(ii) have already averaged over k

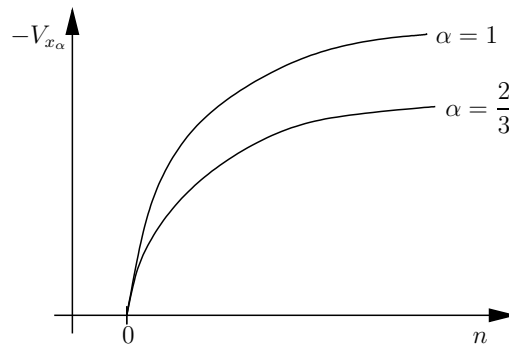
(i)&(ii) can try to approximate further and allow for slowly varying densities
 $n \rightarrow n(r)$

$$\left(\begin{array}{l} \text{Slater's suggestion, } \textit{Phys. Rev.} \mathbf{81}, 385 (1951) \\ \textit{Phys. Rev.} \mathbf{82}, 5381 (1951) \end{array} \right)$$

$$\boxed{V_{x_\alpha}(r) = -\alpha \frac{3}{2\pi} \sqrt[3]{3\pi^2 n(r)} \quad \frac{2}{3} \leq \alpha \leq 1}$$

Remark

- (i) unsatisfactory from theory point of view
- (ii) extremely successful in numerical calculations
- (iii) actual procedure: fit α to reproduce known properties such as the ionization energy



4. Density-Functional Theory

4.1. Thomas-Fermi Theory

Electron density $n(r) = \langle \psi | \sum_{i=1}^N \delta(r - r_i) | \psi \rangle$ (for the moment non-spin polarized systems)

ψ : many-electron ground state

Question: Do we need to know ψ if we want to know n ?

Start from an effective one-particle SE

$$\left\{ -\frac{\nabla^2}{2} + V_{eff}(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r)$$

where V_{eff} may be taken from Hartree or Hartree-Fock-Slater theory

$$\text{here: Hartree} \quad V_{eff}(r) = v(r) + \int \frac{n(r') d^3 r'}{|r - r'|}$$

clear: $SE \rightarrow \psi_i \rightarrow n = \sum_i |\psi_i(r)|^2$, but want to bypass the ψ_i

jellium \Rightarrow wave functions \rightarrow plane waves

$$\varepsilon_i \rightarrow \frac{k^2}{2} + V_{eff}$$

for the uppermost occupied state, i.e., the most weakly bound electron it holds

$$\frac{k_F^2}{2} + V_{eff} = \varepsilon_N = \mu : \quad \text{chem. potential}$$

$$k_F = \sqrt[3]{3\pi^2 n} \quad n = \frac{N}{\Omega}$$

generalize to slowly varying densities $k_F(r) = \sqrt[3]{3\pi^2 n(r)}$

$$\mu = \frac{1}{2}(3\pi^2 n(r))^{\frac{2}{3}} + V_{eff}(r)$$

Thomas-Fermi Equation

where μ : energy of the "fastest" electron;
 μ not spatially dependent (chem. potential!)

⇒ can calculate $n(r)$ for a given μ !
 [F. Bloch, *Z. Physik*, **57**, 545 (1929);
 P. A. M. Dirac, *Proc. Cambridge Phil. Soc.* **26**, 376 (1930)]

Thomas-Fermi equation for jellium equivalent to Hartree if $V_{eff}(r) = v(r) - V_{Hartree}$
 or HFS if $V_{eff}(r) = v(r) + V_{Hartree} + V_{x\alpha}$

For slowly varying potential V_{eff} should be replaced by $\langle \psi_N | V_{eff} | \psi_N \rangle$
 This is not done in the Thomas-Fermi theory → semiclassical approximation

Other approach to Thomas-Fermi

start from Hartree

$$E^e = \sum_i^N \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle + \int d^3r v(r)n(r) \quad (48)$$

$$+ \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|}$$

for jellium:

$$\sum_i^N \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle = \frac{\Omega}{(2\pi)^3} \int_0^{k_F} d^3k \cdot 2 \cdot \frac{k^2}{2} \quad (49)$$

$$= \frac{\Omega \cdot 4\pi}{8\pi^3} \int_0^{k_F} k^4 dk = \frac{\Omega}{2\pi^2} \cdot \frac{1}{5} k^5 \Big|_0^{k_F} = \frac{\Omega}{10\pi^2} k_F^5$$

$$= \frac{\Omega}{10\pi^2} (3\pi^2 n)^{\frac{5}{3}}$$

$$\Rightarrow T_S^{jellium}[n] = \frac{\Omega}{10\pi^2} (3\pi^2 n)^{\frac{5}{3}}$$

$T_S^{jellium}$: functional of kinetic energy of non-interacting particles in jellium approximation

$$\Rightarrow E^e = E^e[n] \quad n = const.$$

i.e. for jellium the energy is a functional of the electron density

Assume(!) variational principle for E , require particle conservation

$$\frac{\delta}{\delta n} \left\{ E^e - \mu \left(\underbrace{\int n(r) d^3r}_{\text{particle conservation}} - N \right) \right\} \stackrel{!}{=} 0$$

$$\text{generalize } T^S \rightarrow T^S[n(r)] = \frac{1}{10\pi^2} \int (3\pi^2 n(r))^{\frac{5}{3}} d^3r$$

$$\text{with } \frac{\delta T^S[n(r')]}{\delta n(r)} = \frac{\partial T^S(n(r'))}{\partial n(r')} \delta(r - r')$$

we obtain

$$\frac{\delta T^S[n(r')]}{\delta n(r)} = \frac{5}{3} \frac{1}{10\pi^2} 3\pi^2 \int (3\pi^2 n(r'))^{\frac{2}{3}} \delta(r - r') d^3r' \quad (50)$$

$$= \frac{1}{2} (3\pi^2 n(r))^{\frac{2}{3}} \quad (51)$$

analogous for other terms in E^e

$$\Rightarrow \boxed{\frac{\delta E^e}{\delta n} \stackrel{!}{=} 0 \quad \Rightarrow \quad \mu = \frac{1}{2} (3\pi^2 n(r))^{\frac{2}{3}} + V_{eff}(r)}$$

Remark

- (i) We have shown that we can obtain the Thomas-Fermi equation from the electronic energy functional, provided there exists a variational principle. We have not shown that such a principle exists!
- (ii) We have only required particle conservation. There should be other important requirements, e.g. $n(r)$ always positive.
- (iii) $n(r)$ is functional of $V_{eff}(r)$ according to Thomas-Fermi equation

$$n(r) = F_1[V_{eff}; \mu]$$

obviously it also holds

$$n(r) = F_2[v(r); \mu]$$

F_2 , however, not explicitly known.

- (iv) starting from here we can obtain Thomas-Fermi theory of screening; beyond our present interest, however

4.2. Hohenberg-Kohn-Theorem

still looking for properties of system described by

$$H^e = \sum_{i=1}^N -\frac{\nabla^2}{2} + \sum_{i=1}^N v(r_i) + \sum_{\substack{i,j \\ i \neq j}}^{N,N} \frac{1}{|r_i - r_j|}$$

assume non-degenerate ground state

$$H^e \Psi = E \Psi$$

non-spin polarized

$$n_{\uparrow}(r) = n_{\downarrow}(r); \quad n(r) = n_{\uparrow}(r) + n_{\downarrow}(r) \quad (52)$$

$$= \langle \Psi \left| \sum_{i=1}^N \delta(r - r_i) \right| \Psi \rangle \quad (53)$$

Hohenberg-Kohn-Theorem:

The expectation value of H^e is a functional of the particle density:

$$E^e[n] = \langle \Psi | H^e | \Psi \rangle = \int v(r) n(r) d^3r + F[n]$$

where $F[n] = \langle \Psi | T^e + V^{ee} | \Psi \rangle$

(P Hohenberg, W Kohn, Phys Rev **136**, B864 (1964); cited 8748 times as of Januar 2012)

Obviously, $\langle \Psi | T^e + V^{ee} | \Psi \rangle$ is functional of Ψ . The fact that it is a functional of $n(r)$ is somewhat surprising.

We will now show that Ψ (\equiv ground state wave function of an arbitrary N -particle problem) is a functional of $n(r)$.

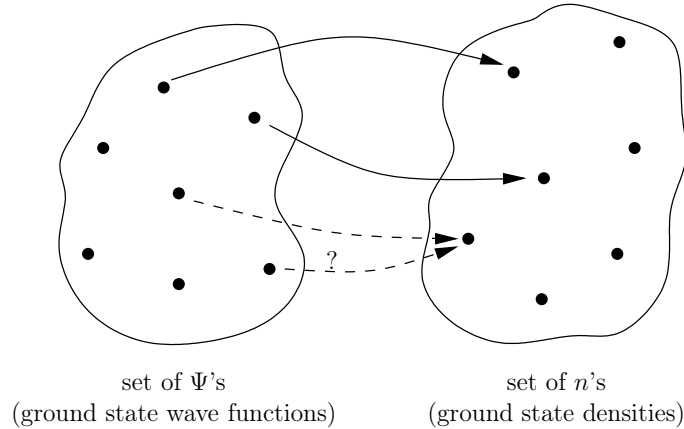
Known: $n(r)$ is functional of Ψ :

$$\Psi \xrightarrow{\langle \sum_{i=1}^N \delta(r-r_i) \rangle} n(r) \quad \text{i.e.} \quad n[\Psi]$$

and E is functional of Ψ :

$$\Psi \xrightarrow{\langle |H^e| \rangle} E \quad \text{i.e.} \quad E = E[\Psi]$$

Question: Is the upper relation, i.e., $\Psi \rightarrow n$, reversible?



three conditions on the elements of set $\{n(r)\}$

- (i) $n(r) \geq 0$
- (ii) $\int n(r) d^3r = N$
- (iii) n continuous

Will now proof the theorem of Hohenberg and Kohn (or the statement $\Psi = \Psi[n]$ respectively)

Proceed according to method "reductio ad absurdum":

Start with two physically different potentials $v(r)$ and $\tilde{v}(r)$, i.e. it holds

$$v(r) - \tilde{v}(r) \neq \text{const.}$$

Solve the Many-body-SE for the two potentials, obtain two ground-state wave functions

$$v(r) \rightarrow H^e \rightarrow \Psi \tag{54}$$

$$\tilde{v}(r) \rightarrow \tilde{H}^e \rightarrow \tilde{\Psi} \tag{55}$$

Because the potentials were different, the wave functions will also be different: $\Psi \neq \tilde{\Psi}$
 Why? Assume both H^e and \tilde{H}^e lead to the same wave function $\Psi = \tilde{\Psi}$

That means

$$(\tilde{H}^e - H^e)\Psi = \sum_{i=1}^N [\tilde{v}(r_i) - v(r_i)]\Psi = (\tilde{E} - E)\Psi.$$

Apart from a discrete amount of points where Ψ equals zero it holds therefore

$$\sum_i [\tilde{v}(r_i) - v(r_i)] = \tilde{E} - E,$$

meaning that $\tilde{v}(r) - v(r) = \text{const.}$, contradicting the starting assumption!

$$\Rightarrow \Psi \neq \tilde{\Psi}$$

Assume now that Ψ and $\tilde{\Psi}$ (even though $\Psi \neq \tilde{\Psi}$) lead to the same $n(r)$. It follows

$$\begin{aligned} E &= \langle \Psi | H^e | \Psi \rangle < \langle \tilde{\Psi} | H^e | \tilde{\Psi} \rangle & (56) \\ & \parallel \\ & \langle \tilde{\Psi} | \tilde{H}^e - \tilde{V} + V | \tilde{\Psi} \rangle \end{aligned}$$

$$\Rightarrow E < \tilde{E} + \underbrace{\langle \tilde{\Psi} \left| \sum_{i=1}^N v(r_i) - \tilde{v}(r_i) \right| \tilde{\Psi} \rangle}_{\int \{v(r) - \tilde{v}(r)\} n(r) d^3r}$$

in an analogous manner we obtain for

$$\tilde{E} = \langle \tilde{\Psi} | \tilde{H}^e | \tilde{\Psi} \rangle \quad (57)$$

$$\tilde{E} < E + \int \{\tilde{v}(r) - v(r)\} n(r) d^3r \quad (58)$$

altogether we have after adding the two equations

$$E + \tilde{E} < \tilde{E} + E$$

i.e. a contradiction!

Thus it is shown that two different ground states Ψ and $\tilde{\Psi}$ lead to two different particle densities $n(r)$ and $\tilde{n}(r)$

Consequences:

- ▶ $E[n]$ is a functional of $n(r)$. Strictly speaking, n should be a member of the set of densities that can be constructed from a ground-state wave function of an arbitrary N -particle Hamiltonian H^e
- ▶ $F[n] = \langle \Psi | T^e + V^{ee} | \Psi \rangle$ is universal in the sense that it does not depend on $v(r)$. This means, for example, that $F[n]$ is the same density functional for atoms, molecules and solids since V^{ee} in all cases, represents the Coulomb repulsion between the electrons

- $E[n]$ reaches under the condition

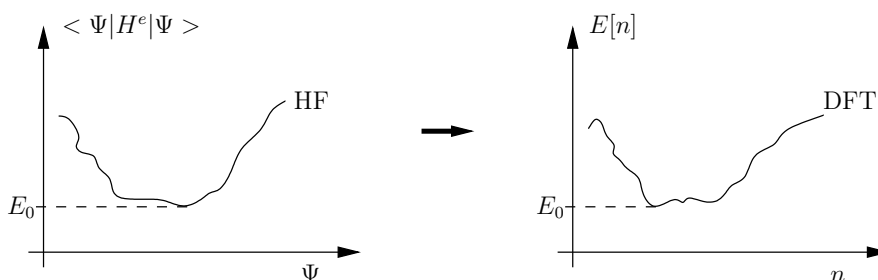
$$\int n(r)d^3r = N$$

a minimum for the correct particle density

- ⇒ The variation principle for $E[\Psi]$ can be formulated as a variation principle for $E[n]$

$$\delta \left\{ E[n] - \mu \left(\int n(r)d^3r - N \right) \right\} = 0$$

Major progress compared to Hartree and HF: There we had to deal with many coordinates, the treatment of which led to many approximations, which had to be made *before* the actual variation. Now we only have to minimize with respect to functions that depend on three coordinates:



4.3. Kohn-Sham Equations

In order to perform the variation Kohn and Sham proposed the following way. We write

$$E[n] = T_S[n] + \int v(r)n(r)d^3r \quad (59)$$

$$+ \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{xc}[n],$$

where $T_S[n]$ stands for the kinetic energy of non-interacting particle. It is known only for jellium systems (cf. Thomas-Fermi theory).

The variation leads to

$$\left. \begin{array}{l} \frac{\delta E}{\delta n} = \mu \\ \parallel \\ \frac{\delta T_S}{\delta n} + V_{eff} \end{array} \right\} \begin{array}{l} \text{equation for non-interacting particles that} \\ \text{move in the potential } V_{eff}(r) \end{array}$$

$$\parallel$$

$$\frac{\delta}{\delta n} \left\{ \int v(r)n(r)d^3r + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{xc} \right\}$$

$$\Rightarrow V_{eff} = v(r) + \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}}{\delta n}$$

Up to now everything is correct. In contrast to Hartree and HF we have first used the variation principle for the ground state and will now think about approximations. In case of Hartree and HF we have **started with an approximation** (Ansatz for wave function) and **then performed the variation**.

We do not know $T_S[n]$, only approximations à la Thomas-Fermi. We do not even know if $T_S[n]$ exists for all densities. We assume it in the following. This assumption is equivalent to restricting the range of densities to the ones which can be represented as

$$n(r) = \sum_i^N |\psi_i(r)|^2,$$

where the ψ_i are the N lowest solutions to an arbitrary single particle Hamiltonian. It is plausible that with these densities we can approximately cover all physically meaningful densities.

How do we now calculate the density of non-interacting particles? We solve the corresponding SE

$$\boxed{\left\{ \frac{\nabla^2}{2} + V_{eff}(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r)}$$

that is known as Kohn-Sham equation. It is to be solved using a self-consistent field method.

We can calculate $T_S[n]$ either via

$$T_S[n] = T_S \left[\sum_i |\psi_i(r)|^2 \right] = \sum_{i=1}^N \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle$$

or

$$T_S[n] = \sum_{i=1}^N \varepsilon_i - \int V_{eff}(r) n(r) d^3r$$

with $n = \sum_i |\psi_i(r)|^2$.

Remarks

- (i) need to calculate single-particle orbitals in order to obtain $T_S[n]$, something we actually wanted to avoid
- (ii) It is not clear whether $T_S[n]$ is an universal functional in n , i.e., independent of $v(r)$. We only know that $F(n) = T_S[n] + E_{xc}[n]$ is an universal functional

As a functional in n we know $T_S[n]$ only for jellium

$$T_S[n] = \frac{\Omega}{(2\pi)^3} \int_{|k| < k_F} \frac{k^2}{2} d^3k = \frac{3}{5} \cdot \frac{1}{2} N (3\pi^2 n)^{\frac{2}{3}}$$

Often useful to introduce the **kinetic energy per particle** $t_S[n]$

$$T_S[n] = \int t_S[n] n(r) d^3r$$

specifically for jellium we obtain

$$t_S = \frac{T_S}{N} = \frac{3}{10} (3\pi^2 n)^{\frac{2}{3}}.$$

For slowly varying densities \rightarrow correction terms in $\nabla n(r)$ (Weizsäcker correction)

$$\frac{\delta T_S[n]}{\delta n} = \frac{1}{2} (3\pi^2 n)^{\frac{2}{3}} = \frac{5}{3} t_S \quad (60)$$

↑

cf. Thomas-Fermi, see derivation above

$\delta T_S/\delta n$ yields the maximum kinetic energy and is therefore larger than t_S

Now we know how to deal with T_S , what about E_{xc} ?

For jellium we can write

$$E_{xc} \left[\frac{N}{\Omega} \right] = \varepsilon_{xc} \left(\frac{N}{\Omega} \right) \cdot N$$

where $\varepsilon_{xc}(n)$ stands for the exchange-correlation energy per particle for a jellium system with density n . Generalize this expression to slowly varying densities

$$E_{xc}[n] = \int \varepsilon_{xc}(n(r))n(r)d^3r + O[\nabla n]$$

”Slowly varying” means that $n(r)$ changes only little on a scale of $\frac{2\pi}{k_F}$. For real systems this requirement is in general not fulfilled, because $\frac{2\pi}{k_F} \approx 0.5 \dots 2\text{\AA}$ is close to typical interatomic distances. Experience shows, however, that the

Local-Density Approximation

$$E_{xc}[n] \rightarrow E_{xc}^{LDA}[n] = \int \varepsilon_{xc}^{LDA}(n(r))n(r)d^3r$$

works nevertheless very well. We will later try to make this plausible.

In order to perform LDA calculations, we need ε_{xc}^{LDA} !

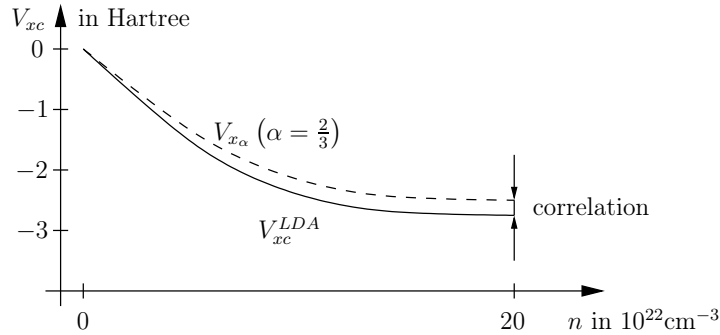
- 1938 Wigner \rightarrow low-density limit
[*Trans. Faraday Soc.* **34**, 678 (1938)]
- 1957 Gell-Mann & Brückner \rightarrow high-density limit
[*Phys. Rev.* **106**, 364 (1957)]
- 1980 Ceperley & Alder \rightarrow intermediate range
[*Phys. Rev. Lett.* **45**, 566 (1980)]
- 1981 Perdew & Zunger \rightarrow parametrization
[*Phys. Rev. B* **23**, 5048 (1981)]

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c$$

$$\varepsilon_x = -0.4582/r_S$$

$$\varepsilon_c = \begin{cases} -0.1423/(1 + 1.0529\sqrt{r_S} + 0.3334r_S) & r_S \geq 1 \\ -0.048 + 0.0311 \ln r_S - 0.0116r_S + 0.002r_S \ln r_S & r_S < 1 \\ n^{-1} = \frac{4\pi}{3}r_S^3 & \end{cases}$$

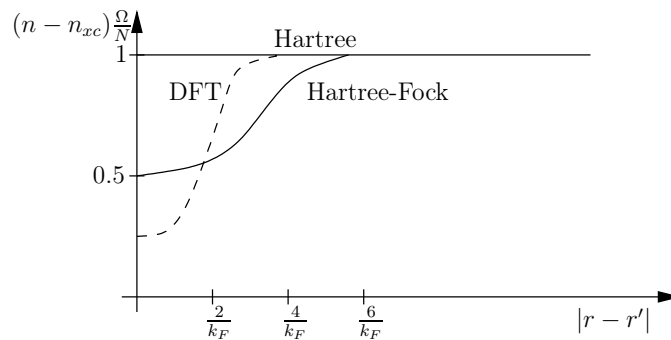
V_{xc}^{LDA} is similar to $V_{x\alpha}$, that explains the success of Hartree-Fock-Slater theory



Slater's Ansatz with $\alpha = \frac{2}{3}$ corresponds to the lower limit for the exchange, $\alpha = 1$ contains more exchange and correlation than the (more exact) density-functional theory

interpretation of exchange-correlation potential of the DFT-LDA

$$V_H + V_{xc} = \int \frac{n(r') - n_{xc}(r, r')}{|r - r'|} d^3r'$$



The exchange-correlation energy is a correction of the Coulomb interaction due to the Hartree term. Thus an electron at r does not interact with particles that are distributed according to $n(r')$, but it feels a distribution $n(r') - n_{xc}(r, r')$. In the vicinity of a particle the density is reduced. The reason for that are the Pauli principle and the Coulomb repulsion.

Surprisingly it turned out that the DFT-LDA delivers excellent results even for systems with strongly varying densities!

Why?

Even though $n_{xc}(r, r')$ has in general the wrong shape, these inaccuracies cancel

partially in the calculation of E_{xc}

$$E_{xc} = -\frac{1}{2} \int \frac{n(r)n_{xc}(r, r')}{|r - r'|} d^3r d^3r'.$$

Multipole expansion of the function $n_{xc}(r, r')$ in the difference coordinate $R \equiv r - r'$

$$n_{xc}(r, r') = \sum_{l,m} n_{lm}^{xc}(r, R) Y_{Lm}(\Omega_R)$$

demonstrates that only the monopole part of the exchange-correlation hole contributes to the xc energy, because we integrate over r' and the interaction potential is isotropic, $\frac{1}{|r-r'|}$.

$\Rightarrow E_{xc}$ depends only on the spherically averaged xc hole

$$\bar{n}_{xc}(r, R) = \frac{1}{4\pi} \int n_{xc}(r, r - R) d\Omega_R$$

$$E_{xc}[n] = -\frac{1}{2} \int n(r) \cdot 4\pi \int_0^\infty \frac{\bar{n}_{xc}(r, R)}{R} R^2 dR d^3r$$

\Rightarrow The xc hole in the LDA does need to describe the true xc hole accurately to yield a good result for E_{xc} . It is sufficient that it provides a reasonable approximation for the spherically averaged xc hole. This has been verified by *Gunnarsson et. al PRB 20, 3136 (1979)* for a series of systems (atoms):

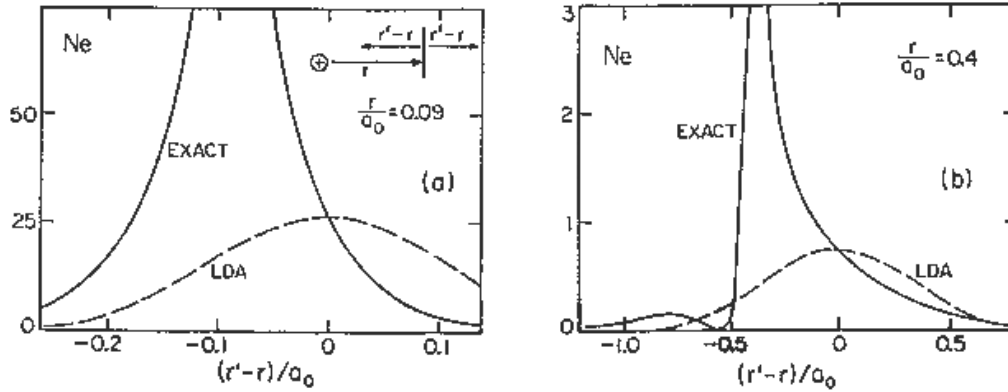


Fig. 7.2 a, b. Exchange hole $q_x(r, r')$ of the Ne atom for (a) $r = 0.09a_0$ and (b) $r = 0.4a_0$. The *full* curves show the exact result while the *dashed* curves depict the result obtained with the local density approximation (from Gunnarsson, Jonson and Lundqvist, 1979)

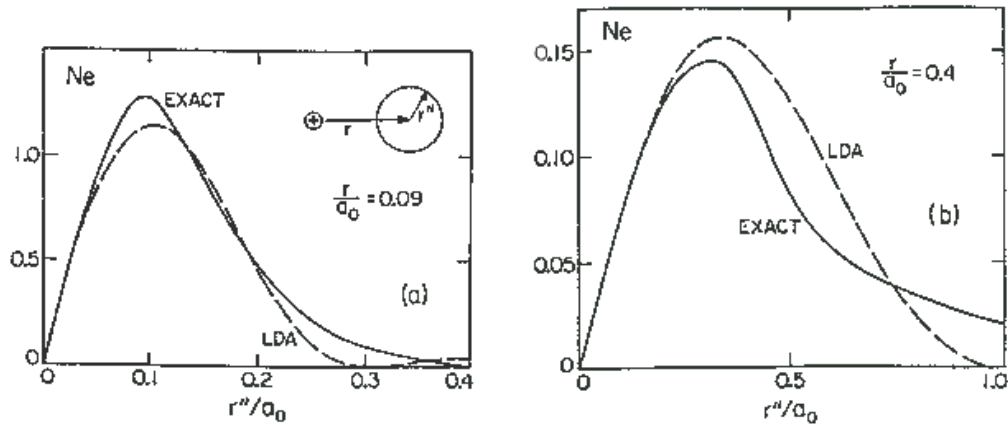


Fig. 7.3 a, b. Spherically averaged exchange hole $(r'' q_{00}^x(r, r'')/\sqrt{4\pi})$ of the Ne atom for (a) $r = 0.09a_0$ and (b) $r = 0.4a_0$. The *solid* curves represent the exact result while the *dashed* curves are obtained from the local density approximation (from Gunnarsson, Jonson and Lundqvist, 1979)

Moreover, n_{xc}^{LDA} fulfills the term rule

$$\int n_{xc}^{LDA}(r, r') d^3 r' = -1.$$

Remark

Sometimes useful to introduce pair correlation function $g(r, r')$ so that

$$E_{xc} = -\frac{1}{2} \int \frac{n(r)(g(r, r') - 1)n(r')}{|r - r'|} d^3 r d^3 r',$$

i.e., $g(r, r')$ related to n_{xc} via

$$n_{xc}(r, r') = n(r')\{g(r, r') - 1\}$$

In LDA we have $g(r, r') = g(|r - r'|)$, which will be wrong in general.

Significance of ε_i in the KS equations?

The meaning of the Kohn-Sham orbitals is itself a very prominent question in DFT theory. While in theory they should not have any physical meaning, empirically it has been observed over and over again that the eigenvalues give a reasonable description of the electron band structure. The eigenvalues in the Hartree-Fock theory were found to represent the energy necessary to add or remove an electron from a given orbital (assuming the correctness of the single-particle description) by Koopman's theorem. A similar theorem was developed by Janak in 1978.

introduce occupation numbers f_i so that

$$0 \leq f_i \leq 1, \quad n = \sum_i f_i |\psi_i(r)|^2$$

and write energy functional in the form

$$E[\psi_1, \dots, \psi_i, \dots] = \sum_i f_i t_i + \int n(r) V_{eff}(r) dr$$

with (following from the KS equation)

$$t_i = -\frac{1}{2} \int \psi_i^*(r) \nabla^2 \psi_i(r) dr = \varepsilon_i - \int \psi_i^*(r) V_{eff}(r) \psi_i(r) dr$$

we obtain

$$\frac{dE}{df_i} = t_i + \int \psi_i^*(r) V_{eff}(r) \psi_i(r) dr$$

i.e.

$$\boxed{\frac{dE}{df_i} = \varepsilon_i} \quad \text{Janak's theorem}$$

[J. F. Janak, *Phys. Rev. B* **18**, 7165 (1978)]

consider now ionization process

$$\Psi^N \rightarrow \Psi^{N-1} + e^- \leftarrow \text{free electron}$$

$$I = E^{N-1} - E^N \tag{61}$$

$$= - \int_0^1 \frac{\partial E}{\partial f_i} df_i = - \int_0^1 \varepsilon_i(f_i) df_i \cong -\varepsilon_i \left(\frac{1}{2} \right) \tag{62}$$

⇒ Calculation with i th level occupied with only half an electron yields approximately the energy required to ionize level i .

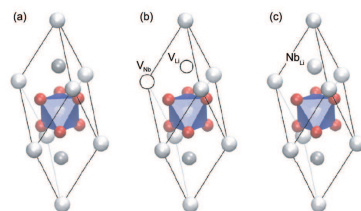
Often relevant for practical calculations, because sometimes more accurate than the difference between two very large numbers, E^{N-1}, E^N .

For delocalized wave functions $\psi_i(r)$ there will be nearly no change in the ε_i upon modifying the $f_i \Rightarrow \varepsilon_i$ correspond to ionization energies

Example: Point defects

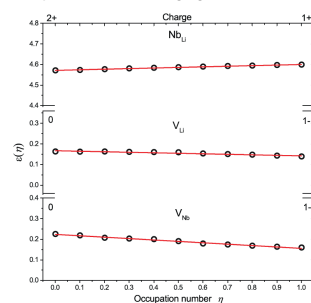
The calculation of charged point defects in solids using periodic boundary conditions is complicated: The total energy of a charged supercell converges slowly with the cell size, so that several energy correction schemes are usually applied to overcome this issue. However, the correction schemes are themselves an approximation and are not universally applicable. The Janak theorem provides an alternative method to determine charge transition levels which does not require to compare the total energies of differently charged systems. It is therefore less affected from issues arising from the supercell approach. Shown below is a recent application to lithium niobate point defects. Shown are the defect structures, the nearly linear dependence of the Kohn-Sham HOMO in dependence on the occupation number (prerequisite for the application of Janak's theorem, and the calculated defect formation energies.

structure models for lithium niobate point defects

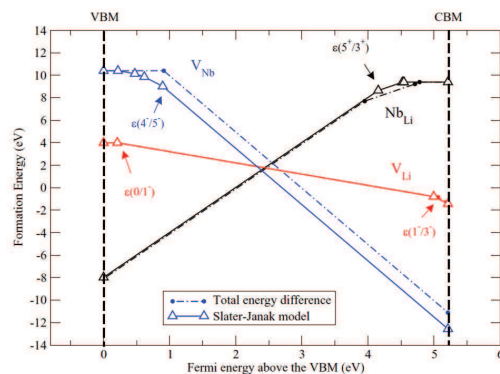


Y Li, S Sanna, WG Schmidt
 "Modeling intrinsic defects in LiNbO₃ within the Slater-Janak transition model"
J. Chem. Phys. 140, 234113 (2014)

change of Kohn-Sham eigenvalue (HOMO) in response to defect charging



defect formation energies in dependence on the Fermi level position calculated using the Janak theorem in comparison to total-energy differences



Example: Hydrogen atom
 in LDA we have SE

$$\left\{ -\frac{\nabla^2}{2} - \frac{1}{r} + \underbrace{\int \frac{|\psi_1(r')|^2}{|r-r'|} d^3r'}_{:=0 \text{ for exact calculation}} + V_{xc}(r) \right\} \psi_1(r) = \varepsilon_1 \psi_1$$

$\varepsilon_1 = -13.6 \text{ eV}$ (exact)

$\varepsilon_1^{LDA} = -6.4 \text{ eV} \Rightarrow$ LDA obviously very bad

$I^{LDA} = -\varepsilon_1^{LDA} \left(\frac{1}{2}\right) = 12.4 \text{ eV}$ rather close to exact ionization energy

Spin Polarization

$$n(r) = n_{\uparrow}(r) + n_{\downarrow}(r) \quad n_{\uparrow}(r) = \sum_{i=1}^N \delta_{S_i, \uparrow} |\psi_i(r)|^2$$

$$n_{\downarrow}(r) = \sum_{i=1}^N \delta_{S_i, \downarrow} |\psi_i(r)|^2$$

single-particle equation

$$\left\{ -\frac{\nabla^2}{2} + V_{eff_{S_i}}(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r)$$

with effective potential that depends on n_{\uparrow} and n_{\downarrow}

$$V_{eff_{S_i}}(r) = v(r) + \int \frac{n(r')}{|r-r'|} d^3r' + V_{x_{S_i}}(r) + V_c(r)$$

Correlation is the same as in DFT, exchange, however, depends on the spin orientation.

For practical calculations local spin density approx. (LSDA)

$$E_{xc}^{LSDA} = \int \varepsilon_{xc}(n, m) n(r) d^3r$$

where $\varepsilon_{xc}(n, m)$ is the exchange and correlation energy per particle for a homogeneous electron gas with density n and magnetization m .

$$m(r) = \mu_B \cdot \{n_{\uparrow}(r) - n_{\downarrow}(r)\}$$

Example: ionization energy of H atom in LSDA

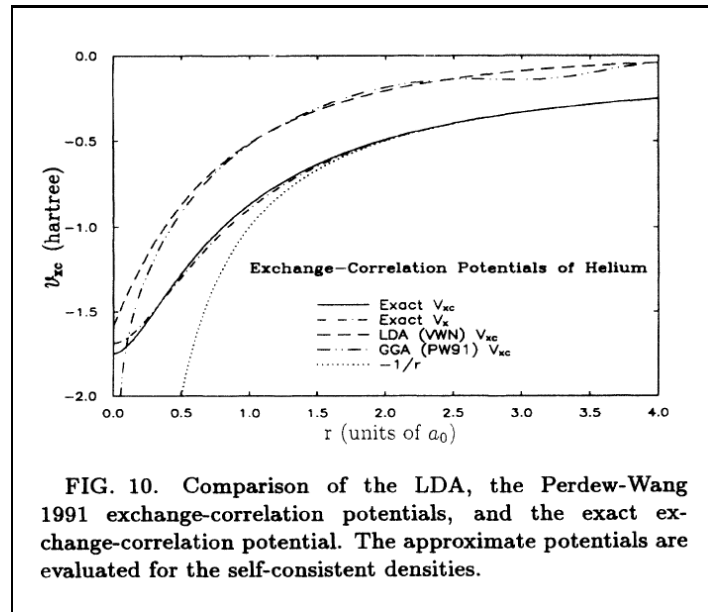
$$I^{LSDA} = 13.4 \text{ eV!}$$

4.4. XC functionals

In the previous section 4.3 we introduced the local-density approximation (LDA) to the xc energy of an inhomogeneous electron gas

$$E_{xc}^{LDA} = \int \epsilon_{xc}^{LDA}(n(r))n(r)dr \quad (63)$$

One of the major short comings of the LDA is that it is not free of self-interaction, and therefore has the wrong asymptotic behaviour. Rather than going like $-\frac{1}{r}$ for $r \rightarrow \infty$, the LDA xc potential goes to zero exponentially fast, since the density in a finite system drops off exponentially. However, if an electron ventures far away into the other regions of the system, leaving $N - 1$ electrons behind, it should see the Coulomb potential of the remaining negative ion, and it is the job of the xc potential to take care of this. The problem is illustrated, e.g, in the work of Umrigar and Gonze, Phys. Rev. A, **50**, 3827 (1994), see figure below.



While the wrong asymptotics (caused by spurious self-interactions) has relatively mild consequences for integrated quantities such as the total energy, it is still a severe problem

- The Kohn-Sham energy eigenvalues come out too low in magnitude. In particular, the LDA eigenvalue of the highest occupied orbital differs by 30-50 % from the ionization energy.

- The LDA does not produce stable negative ions, since the potential is too shallow to bind an extra electron.
- LDA band gaps in solids are typically off by a considerable amount.
- While the LDA generally captures the right physical trends, it is not accurate enough for many chemical applications.

The idea of improving the LDA by constructing xc functionals which depend not only on the local density itself but also on its gradients has a long history and goes back to the original work by Hohenberg and Kohn from 1964.

Generalized gradient approximations (GGA) are a class of xc functionals which have the following structure

$$E_{xc}^{GGA}[n \uparrow, n \downarrow] = \int dr e_{xc}^{GGA}(n \uparrow(r), n \downarrow(r), \nabla n \uparrow(r), \nabla n \downarrow(r)). \quad (64)$$

They do not arise from systematic order-by-order expansions in terms of the density gradients. Rather, the idea is to construct ϵ_{xc}^{GGA} in such a way that it satisfies as many of the known exact properties of $\epsilon_{xc}[n]$ as possible. As there is no unique prescription for doing so, there are hundreds of GGA functionals available now.

See Sousa, Fernandes, Ramos \Rightarrow J. Phys. Chem. A **111**, 1043a (2007) for a recent overview.

Examples: The exchange functional B88 is given by

$$E_x^{B88}[n \uparrow, n \downarrow] = E_x^{LDA}[n \uparrow, n \downarrow] - \beta \sum_{\sigma} \int dr n_{\sigma}^{\frac{4}{3}} \frac{x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1}(x_{\sigma})} \quad (65)$$

$$\text{where } x_{\sigma} = \frac{|\nabla n_{\sigma}(r)|}{n_{\sigma}^{\frac{4}{3}}(r)} \text{ and } \beta = 0.0042 \quad (66)$$

[Becke, Phys. Rev. A **38**, 3098 (1988)]

The correlation energy functional of Lee, Young and Parr [Phys. Rev. B **37**, 785 (1988)] reads

$$E_c^{LYP}[n] = -a \int \frac{dr}{1 + n \cdot d} \left(n + b \cdot n^{\frac{1}{3}} [C_F n^{\frac{5}{3}} - 2t_{\omega} + \frac{1}{9}(t_{\omega} + \frac{\nabla^2}{2}n)e^{-cn^{-\frac{1}{3}}}] \right) \quad (67)$$

where

$$\begin{aligned}
 C_F &= \frac{3}{10}(3\pi^2)^{\frac{2}{3}} & (68) \\
 t_\omega &= \frac{1}{8}\left(\frac{|\nabla n|^2}{n} - \nabla^2 n\right) \\
 a &= 0.0049, \quad b = 0.132, \quad c = 0.2533
 \end{aligned}$$

Combining the Becke and Lee-Young-Parr functionals yields the popular GGA known as BLYP.

Very popular is also the PBE functional [Perdew, Burke, Ernzerhof, Phys. Rev. Lett. **79**, 3865 (1996); *ibid.* **78**, 1396 (1997)].

$$\begin{aligned}
 E_x^{PBE}[n] &= \int dr e_x^h(n) \left[1 + k - \frac{k}{1 + \beta\pi^2 s^2 / 3k}\right] & (69) \\
 \text{where } k &= 0.804, \beta = 0.066725, s = \frac{|\nabla n|}{2n \cdot k_F}
 \end{aligned}$$

from the above functional a spin-dependent version is obtained by

$$E_x[n \uparrow, n \downarrow] = \frac{1}{2} E_x[2n \uparrow] + \frac{1}{2} E_x[2n \downarrow]. \quad (70)$$

The PBE correlation energy is given by

$$\begin{aligned}
 E_c^{PBE}[n, \xi] &= \int dr [e_c^h(n, \xi) + nc_0 \phi^3 x \ell n \left\{1 + \frac{(1 + At^2)\beta t^2 / c_0}{1 + At^2 + A^2 t^4}\right\}] & (71) \\
 \text{where } f &= \frac{|\nabla n|}{4n\sqrt{\frac{K_F}{\pi}}}, \quad c_0 = 0.031091 \\
 \phi &= \frac{1}{2}[(1 + \xi)^{\frac{2}{3}} + (1 - \xi)^{\frac{2}{3}}], \\
 A &= \frac{\beta/c_0}{e - \frac{e_c(r_s \xi)}{c_0 \phi^3} - 1}, \quad \xi = \frac{n \uparrow - n \downarrow}{n}
 \end{aligned}$$

Compared with GGA xc energies, which tend to agree very well with exact results, GGA xc potentials tend to be of much poorer quality. In particular, they do not have the correct asymptotic behaviour $-\frac{1}{r}$.

In order to further improve the functionals, so-called **meta-GGAs** were introduced that include additional elements such as Laplacians of the spin densities and Kohn-Sham orbital kinetic-energy densities

$$E_{xc}^{MGGA} = \int dr \epsilon_{xc}^{MGGA}(n \uparrow, n \downarrow, \nabla n \uparrow, \nabla n \downarrow, \nabla^2 n \uparrow, \nabla^2 n \downarrow, \tau \uparrow, \tau \downarrow) \quad (72)$$

$$\text{where } \tau_{\sigma}(r) = \frac{1}{2} \sum_{j=1}^{occ} |\nabla \varphi_{j\sigma}(r)|^2.$$

A major advantage of these functionals is that they are partially free of self-interaction. A serious complication of meta-GGAs is that the kinetic-energy density τ is not an explicit functional of the density. Therefore the functional derivative $v_{xc} = \frac{\delta E_{xc}}{\delta n}$ cannot be evaluated directly.

The next level of refinement is achieved with **hyper-GGAs** and **hybrid functionals** by incorporating the exact exchange-energy density

$$e_x^{exact}(r) = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{N\sigma} \int dr' \frac{\varphi_{i\sigma}^*(r') \varphi_{j\sigma}(r') \varphi_{j\sigma}^*(r)}{|r - r'|} \quad (73)$$

Like the kinetic-energy density, e_x^{exact} is an implicit density functional, but an explicit orbital functional. Hybrid functionals are constructed by mixing a fraction of the exact exchange energy functional with a standard LDA or GGA in the following way:

$$E_{xc}^{hybrid} = a E_x^{exact} + (1 - a) E_x^{GGA} + E_c^{GGA} \quad (74)$$

where the semiempirical constant a has a value of around 0.25. The PBE0 functional is obtained by substituting the PBE functional into the equation above. The most popular hybrid functional today is the three-parameter functional B3LYP

$$E_{xc}^{B3LYP} = (1 - a) E_x^{LDA} + a E_x^{exact} + b(E_x^{B88} - E_x^{LDA}) + c E_E^{LYP} + (1 - c) E_c^{LDA} \quad (75)$$

with $a = 0.20$, $b = 0.72$, and $c = 0.81$.

In 2007 about 80 % of all DFT applications were performed with B3LYP. However, B3LYP does not work for everything: since the LYP correlation does not reproduce the correct limit for the homogeneous system, B3LYP fails for free-electron-like metallic systems. A particular class of hybrid functionals, called **range-separated hybrids**, has attracted much interest lately, see e.g. [Baer, Livshits, Salzner, Annu. Rev. Phys. Chem. **61**, 85 (2010)].

The basic idea is to separate the Coulomb interaction into a short-range (SR) and a long-range (LR) part:

$$\frac{1}{|r-r'|} = \frac{f(\mu|r-r'|)}{|r-r'|} + \frac{1-f(\mu|r-r'|)}{|r-r'|} \quad (76)$$

where the function f has the properties $f(\mu x \rightarrow 0) = 1$ and $f(\mu x \rightarrow \infty) = 0$, common examples are

$$f(\mu x) = e^{-\mu x} \quad (77)$$

or

$$f(\mu x) = \operatorname{erf}(\mu x) = \frac{2}{\sqrt{\pi}} \int_0^{\mu x} dx' e^{-x'^2}$$

where the separation parameter μ is determined either empirically, or using physical arguments. The range-separated hybrid xc functional then has the following generic form

$$E_{xc} = E_x^{SR-DFA} + E_x^{LR-HF} + E_c^{DFA} \quad (78)$$

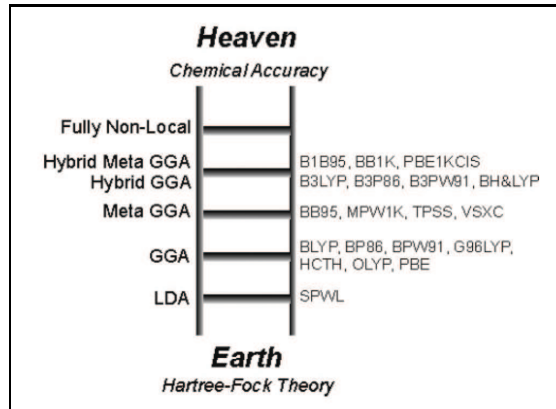
where DFA stands for any standard density-functional approximation to the exchange or correlation energy, such as LDA or GGA. The main strength of range-separated hybrid functionals is that they produce effective potentials with the correct long-range asymptotic behaviour! This leads to a significant improvement in polarizabilities, bond dissociations and charge-transfer excitations.

Range-separated hybrids work in the asymptotic range, but problems at short distances remain. What can we do to improve the description of correlation? Unoccupied orbitals are included to better describe the correlation energy via many-body schemes. So-called **double hybrid functionals** such as B2PLYP incorporate correlations at a second-order perturbative level (MP2)

$$E_{xc} = (1-a)E_x^{GGA} + aE_x^{exact} + bE_c^{GGA} + cE_c^{MP2}. \quad (79)$$

While MP2-based double hybrids have become popular in the chemistry community, the preferred approach in physics is the random-phase approximation (RPA) to correlation.

Below the Jacob's ladder for the five generation of DFT functionals with indication of some of the most common DFT functionals within each rung is shown, from SF Soussa *et al.* J. Phys. Chem. A **111**, 10439 (2007).



5. Time-Dependent Density-Functional Theory

5.1. Runge-Gross Theorem

The time-dependent Schrödinger equation defines a map by which each external potential $v(r, t)$ produces a time-dependent wave function $\psi(t)$ for a given initial state ψ_0 . A second map generates a density $n(r, t)$ from $\psi(t)$:

$$v(r, t) \xrightarrow[\text{fixed } \psi_0]{i\frac{\delta\psi}{\delta t} = \hat{H}(t)\psi} \psi(t) \xrightarrow{\langle \psi(t) | \hat{n} | \psi(t) \rangle} n(r, t) \quad (80)$$

Physically, this means that the dynamics of the system is determined by the time-dependent potential via the SE. To construct a time-dependent DFT, the map needs to be turned around: we need to show that the time-dependent density $n(r, t)$ is equally valid as a variable which completely determines the dynamics of the system. It must be proved that there is a unique, one-to-one correspondence between time-dependent densities and potentials. This correspondence is secured by the

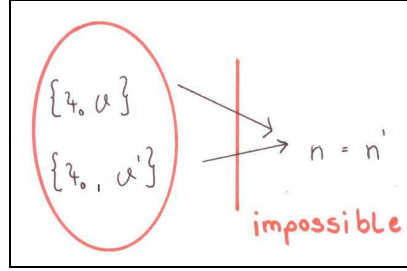
Runge-Gross Theorem: For a fixed initial state and given an analytic time dependent potential, the mapping to the time dependent density is injective. That is, for the same initial state, two different external potentials cannot give the same density function $n(r, t)$.

Analytic time dependent potential means that the potential can be expanded in a Taylor series about the initial value

$$v(r, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(r) (t - t_0)^k \quad (81)$$

The statement that two potentials v and v' differ by more than a function $c(t)$ can be expressed through the requirement that there exists a smallest integer $k \geq 0$ such that

$$v_k(r) - v'_k(r) \neq \text{const.}$$



(E Runge, EKV Gross, Phys Rev Lett **52**, 997 (1984); cited 2057 times as of Jan 2012)

Proof:

Many-body current density given by

$$\begin{aligned}
 j(r) &= -\frac{i}{2} \sum_i^N \int \prod_j^N dr_j \delta(x_i - x) \left\{ \psi^*(r_1, \dots, r_N) \nabla_i \psi(r_1, \dots, r_N) - \psi(r_1, \dots, r_N) \nabla_i \psi^*(r_1, \dots, r_N) \right\} \\
 &= -\frac{iN}{2} \int dr_{2\dots N} \left\{ \psi^*(r, r_2, \dots, r_N) \nabla \psi(r, r_2, \dots, r_N) - \psi(r, r_2, \dots, r_N) \nabla \psi^*(r, r_2, \dots, r_N) \right\}
 \end{aligned} \tag{82}$$

It obeys the continuity relation

$$\frac{\partial}{\partial t} n(r) = -\nabla \cdot j(r) \tag{83}$$

The equation of motion for the current density is

$$\begin{aligned}
 \frac{\partial}{\partial t} j &= -\frac{iN}{2} \int dr_{2\dots N} \frac{\partial}{\partial t} (\psi^* \nabla \psi - \psi \nabla \psi^*) \\
 &= -\frac{iN}{2} \int dr_{2\dots N} \left(\underbrace{\frac{\partial \psi^*}{\partial t}}_{iH\psi^*} \cdot \nabla \psi + \psi^* \nabla \underbrace{\frac{\partial \psi}{\partial t}}_{-iH\psi} - \underbrace{\frac{\partial \psi}{\partial t}}_{-iH\psi} \nabla \psi^* - \psi \nabla \underbrace{\frac{\partial \psi^*}{\partial t}}_{iH\psi^*} \right) \\
 &= \frac{N}{2} \int dr_{2\dots N} ((H\psi^*) \nabla \psi - \psi^* \nabla H\psi + (H\psi) \nabla \psi^* - \psi \nabla (H\psi^*))
 \end{aligned} \tag{84}$$

We now consider the difference of the two current densities j and j' related to different potentials $V = \sum_j v(r_j)$ and $V' = \sum_j v'(r_j)$

$$\begin{aligned} & \left. \frac{\partial}{\partial t} (j(r, t) - j'(r, t)) \right|_{t=0} \tag{85} \\ &= \frac{N}{2} \int dr_{2\dots N} \left((V - V') \psi^* \nabla \psi - \psi^* \nabla ((V - V') \psi) + (V - V') \psi \nabla \psi^* - \psi \nabla ((V - V') \psi^*) \right) \Big|_{t=0} \end{aligned}$$

employ product rule of differentiation

$$\begin{aligned} &= -\frac{N}{2} \int dr_{2\dots N} \left(\psi^* (\nabla(V - V')) \psi + \psi (\nabla(V - V')) \psi^* \right) \Big|_{t=0} \\ &= -N \int dr_{2\dots N} |\psi|^2 \underbrace{\nabla(V - V')}_{\nabla_1 \underbrace{\sum_j v(r_j) - v'(r_j)}_{\nabla_1 (v(1) - v'(1)) = \nabla(v(r) - v'(r))}} \\ &= -n(r, 0) \nabla(v(r, 0) - v'(r, 0)) \end{aligned}$$

If the potentials differ by more than a time dependent function at $t = 0$ the first derivatives of the current densities j and j' differ, and therefore the current densities will become different, provided

$$v_k(r) - v'_k(r) \neq \text{const.} \tag{86}$$

holds for $k = 0$. If the smallest integer k for which the above condition is satisfied is greater than zero, then the first derivatives of the currents are equal, and the difference between j and j' shows up in higher derivatives. We then get

$$\left. \frac{\partial^{k+1}}{\partial t^{k+1}} (j(r, t) - j'(r, t)) \right|_{t=0} = -n(r, 0) \nabla \left(\frac{\partial^k}{\partial t^k} (v(r, 0) - v'(r, 0)) \right) \tag{87}$$

We therefore conclude that $j(r, t) \neq j'(r, t)$ for $t > 0$. Next we need to show that having different current densities means that the densities themselves are different. We define the function

$$\omega_k(r) = \frac{\partial^k}{\partial t^k} (v(r, 0) - v'(r, 0)) \tag{88}$$

and use the continuity relation

$$\frac{\partial^{k+2}}{\partial t^{k+2}}(n(r, t) - n'(r, t)) \Big|_{t=0} = \underbrace{-\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}}(j - j') \Big|_{t=0}}_{\omega_k(r)} + \underbrace{\nabla \cdot n(r, 0) \nabla \left(\frac{\partial^k}{\partial t^k}(v(r, 0) - v'(r, 0)) \right) \Big|_{t=0}}_{\omega_k(r)} \quad (89)$$

It suffices to show that

$$\nabla \cdot (n(r, 0) \nabla \omega_k(r)) \neq 0 \quad (90)$$

consider the integral

$$\int dr \nabla \cdot (\omega_k n \nabla \omega_k) \stackrel{\uparrow}{=} \int dr n (\nabla \omega_k)^2 + \int dr \omega_k \nabla \cdot (n \nabla \omega_k) \quad (91)$$

$\parallel \leftarrow$ Gauss product rule

$$\oint dA \cdot (\omega_k n \nabla \omega_k)$$

\parallel

$$0 \left(\text{provided we integrate far enough and the potential dies fast enough, i.e. as } \frac{1}{r} \right)$$

Because $n(\nabla \omega_k)^2 \geq 0$, for different potentials it holds

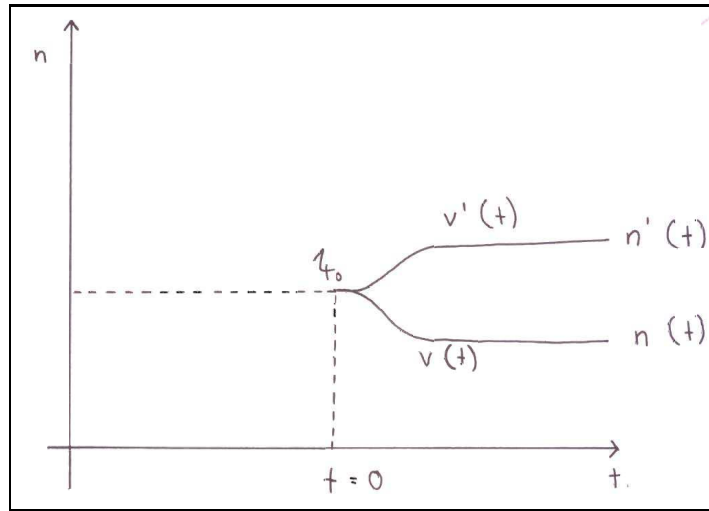
$$\int dr n (\nabla \omega_k)^2 > 0 \quad (92)$$

Therefore

$$\begin{aligned} \int dr \omega_k \nabla \cdot (n \nabla \omega_k) &\neq 0 \\ \implies \nabla \cdot (n(r, 0) \nabla \omega_k(r)) &\neq 0 \end{aligned} \quad (93)$$

We have thus shown that the densities are different infinitesimally later than $t = 0$, see illustration below

This is the fundamental existence theorem of TDDFT: from the one-to-one correspondence, it follows immediately that the time-dependent density is a unique functional of the potential, but also, vice versa, that the external potential is a unique functional of the time-dependent density (for a given fixed initial state). This means that the many-body Hamiltonian $H(t)$ and thus the many-body wave function $\psi(t)$ are functionals of $n(r, t)$ as well:



$$\begin{aligned}
 v(r, t) = v[n, \psi_0](r, t) &\Rightarrow H(t) = H[n, \psi_0](t) \\
 &\Rightarrow \psi(j) = \psi[n, \psi_0](t)
 \end{aligned}
 \tag{94}$$

Here we have explicitly indicated the dependence on the fixed initial state ψ_0 . As an immediate consequence, we deduce that all physical observables become functionals of the density

$$O(t) = \langle \psi[n, \psi_0] | O | \psi[n, \psi_0] \rangle = O[n, \psi_0](t) \tag{95}$$

This tells us that, at least on a formal level, the time-dependent density is all we need to obtain any desired observable of a time-dependent many-particle system.

5.2. The time-dependent Kohn-Sham equation

According to the Runge-Gross theorem there is a one-to-one correspondence between the time-dependent external potential $v(r, t)$ and the time-dependent electron density $n(r, t)$ for a fixed initial state. This can be seen as a generalization of the Hohenberg-Kohn theorem for electronic ground states. Similar to the static case, one can cast the many-electron problem into the Kohn-Sham non-interacting electron system assuming that the density of the interacting system can be reproduced by a non-interacting effective potential. This assumption was proven by van Leeuwen (Phys.Rev.Lett. **82**, 3863 (1999)).

The density is then given by

$$n(r, t) = \sum_i^{\text{occ}} |\phi_i(r, t)|^2 \quad (96)$$

where the orbitals $\phi_i(r, t)$ satisfy the time-dependent Kohn-Sham equations

$$i \frac{\partial}{\partial t} \phi_i(r, t) = \left(-\frac{\nabla^2}{2} + v_s[n](r, t) \right) \phi_i(r, t) \quad (97)$$

with

$$v_s[n](r, t) = v_{\text{ext}}(r, t) + \int dr' \frac{n(r', t)}{|r - r'|} + v_{xc}[n](r, t) \quad (98)$$

In the usual **adiabatic approximation** the exchange-correlation potential is taken to be simply the derivative of the static ground state exchange-correlation energy, E_{xc} , with respect to the density

$$v_{xc}[n](r, t) \approx \left. \frac{\delta E_{xc}}{\delta n} \right|_{n=n(r,t)}. \quad (99)$$

In practical applications one utilizes one of the many available approximate static xc functionals $E_{ex}[n(r)]$ such as one of the various forms of LDA/GGA.

The probably most widely used example of this class of time-dependent xc potentials is the **adiabatic local-density approximation** (ALDA)

$$v_{xc}^{\text{ALDA}}(r, t) = \left. \frac{de_{xc}^h(\bar{n})}{d\bar{n}} \right|_{\bar{n}=n(r,t)} \quad (100)$$

where $e_{xc}^h(\bar{n})$ is the xc energy density of a homogeneous electron liquid of particle density \bar{n} . Notice that there are two levels of approximations involved here

- we use a functional from static DFT and evaluate it with a time-dependent density, thus ignoring any memory effects
- the static xc functional itself is of course an approximation, too.

5.3. Linear density response in TDDFT

Consider a time-dependent external potential of the form

$$v_{\text{ext}}(r, t) = v_0(r) + v_1(r, t)\theta(t - t_0), \quad (101)$$

i.e., the system is in its ground state for $t \leq t_0$ and $v_1(r, t)$ is a small time-dependent perturbation switched on at t_0 .

The initial many-body ground state is uniquely determined due to the Hohenberg-Kohn-Sham theorem of static DFT, and, according to the Runge-Gross theorem, there exists a unique one-to-one correspondence between $v(r, t)$ and $n(r, t)$. Therefore we can write the time-dependent density as a functional of the external potential

$$n(r, t) = n[v_{ext}](r, t). \quad (102)$$

We expand the density response in powers of the perturbation v_1

$$n(r, t) - n_0(r) = n_1(r, t) + n_2(r, t) + \dots \quad (103)$$

The first-order density response is given by

$$n_1(r, t) = \int dt' \int dr' \chi(r, t, r', t') v_1(r', t'), \quad (104)$$

where $\chi = \chi_{nn}$ is the density-density response function (cf. Appendix A). It can be calculated from the Taylor expansion of the density response as

$$\chi(r, t, r', t') = \left. \frac{\delta n[v_{ext}](r, t)}{\delta v_{ext}(r', t')} \right|_{v_0(r)}. \quad (105)$$

The time-dependent density $n(r, t)$ corresponding to $v_{ext}(r, t)$ can also be reproduced in a non-interacting, time-dependent Kohn-Sham system with the effective potential

$$v_s[n](r, t) = v_{ext}(r, t) + \underbrace{\int dr' \frac{n(r', t)}{|r - r'|}}_{v_H(r, t)} + v_{xc}[n](r, t) \quad (106)$$

and a density-density response function for non-interacting Kohn-Sham particles

$$\chi_s(r, t, r', t') = \left. \frac{\delta n[v_s](r, t)}{\delta v_s(r', t')} \right|_{v_s[n_0](r)}. \quad (107)$$

We now calculate (see Appendix B for the definition and calculation of functional derivatives)

$$\begin{aligned}
 n_1(r, t) &= \int dt' \int dr' \underbrace{\chi(r, t, r', t')}_{\parallel} v_1(r', t') & (108) \\
 &\quad \parallel \\
 &\quad \frac{\delta n(r, t)}{\delta v_{ext}(r', t')} \\
 &\quad \parallel \\
 &\quad \int dr'' \int dt'' \underbrace{\frac{\delta n(r, t)}{\delta v_s(r'', t'')}}_{= \chi_s(r, t, r'', t'')} \cdot \underbrace{\frac{\delta v_s(r'', t'')}{\delta v_{ext}(r', t')}}_{= A}
 \end{aligned}$$

$$A = \delta(r'' - r')\delta(t'' - t') \quad (109)$$

$$\begin{aligned}
 &+ \int dr''' \int dt''' \left\{ \underbrace{\frac{\delta v_H(r'', t'')}{\delta n(r''', t''')}}_{\frac{1}{|r'' - r'''|}\delta(t'' - t''')} \frac{\overbrace{\chi(r''', t''', r', t')}}{\delta v_{ext}(r', t')} + \underbrace{\frac{\delta v_{xc}(r'', t'')}{\delta n(r''', t''')}}_{=: f_{xc}(r'', t'', r''', t''')} \cdot \underbrace{\frac{\delta n(r''', t''')}{\delta v_{ext}(r', t')}}_{\chi(r''', t''', r', t')} \right\} \\
 &\quad \text{time-dependent xc} \\
 &\quad \text{kernel} \\
 &= \delta(r'' - r')\delta(t'' - t') + \int dr''' \int dt''' \chi(r''', t''', r', t') \left\{ \frac{\delta(t'' - t''')}{|r'' - r'''|} + f_{xc}(r'', t'', r''', t''') \right\} & (110)
 \end{aligned}$$

exploiting that $\int dt' \int dr' \chi(r''', t''', r', t') v_1(r', t') = n_1(r''', t''')$ we obtain

$$n_1(r, t) = \int dt' \int dr' \chi_s(r, t, r', t') [v_1(r', t') + \int dt'' dr'' \left\{ \frac{\delta(t' - t'')}{|r' - r''|} + f_{xc}(r', t', r'', t'') \right\} n_1(r'', t'')] \quad (111)$$

This equation shows that the linear density response must be calculated self-consistently, since the effective potential on the right-hand side depends on $n_1(r, t)$. The interacting and non-interacting response functions depend only on the time difference $t - t'$ (see Appendix A), therefore we can carry out the Fourier transformation of the above equation and obtain

$$\begin{aligned}
 n_1(r, \omega) &= \int dr' \chi_s(r, r', \omega) \underbrace{\left[v_1(r', \omega) + \int dr'' \left\{ \frac{1}{|r' - r''|} + f_{xc}(r', r'', \omega) \right\} n_1(r'', \omega) \right]}_{=: v_{s1\dots} \text{ linearized effective potential}} & (112)
 \end{aligned}$$

The frequency-dependent, non-interacting Kohn-Sham response function is given by

$$\chi_s(r, r', \omega) = \sum_{j,k=1}^{\infty} (f_k - f_j) \frac{\varphi_j^0(r) \varphi_k^{0*}(r') \varphi_j^0(r') \varphi_k^0(r')}{\omega - \omega_{jk} + i\eta} \quad (113)$$

where f_i and f_k are the occupation members of the Kohn-Sham ground state orbitals and $\omega_{jk} = \epsilon_j - \epsilon_k$ are difference between Kohn-Sham energy eigen values.

5.4. The Casida equation

Linear-response TDDFT is most commonly applied in an explicitly spin-dependent formulation. The linear spin-density response is given by

$$n_{1\sigma}(r, \omega) = \sum_{\sigma'} \int dr' \chi_{s,\sigma\sigma'}(r, r', \omega) v_{s1\sigma'}(r', \omega) \quad (114)$$

with the spin-dependent linearized effective potential

$$v_{s1\sigma}(r, \omega) = v_{1\sigma}(r, \omega) + \sum_{\sigma'} \int dr' \left\{ \frac{1}{|r - r'|} + f_{xc,\sigma\sigma'}(r, r', \omega) \right\} n_{1\sigma'}(r', \omega) \quad (115)$$

and the non-interacting Kohn-Sham response

$$\chi_{x,\sigma,\sigma'}(r, r', \omega) = \delta_{\sigma\sigma'} \sum_{j,k=1}^{\infty} (f_{k\sigma} - f_{j\sigma}) \frac{\varphi_{j\sigma}^0(r) \varphi_{k\sigma}^{0*}(r) \varphi_{j\sigma}^{0*}(r') \varphi_{k\sigma}^0(r')}{\omega - \omega_{jk\sigma} + i\eta} \quad (116)$$

which is diagonal in the spin indices. For notational convenience we define the combined Hartree-xc Kernel as

$$f_{Hxc,\sigma\sigma'}(r, r', \omega) = \frac{1}{|r - r'|} + f_{xc,\sigma\sigma'}(r, r', \omega) \quad (117)$$

where $f_{xc,\sigma\sigma'}$ is the Fourier transform of

$$f_{x,\sigma\sigma'}(r, t, r', t') = \frac{\delta v_{xc}[n \uparrow, n \downarrow](r, t)}{\delta n_{\sigma'}(r', t')} \Big|_{n_{0\uparrow}(v)}^{n_{0\downarrow}(v)} \quad (118)$$

We thus obtain the linear spin-density response

$$n_{1\sigma}(r, \omega) = \sum_{\sigma'} \int dr' \chi_{s,\sigma\sigma'}(r, r', \omega) \left\{ v_{1\sigma}(r', \omega) + \sum_{\sigma''} \int dr'' f_{Hxc,\sigma'\sigma''}(r', r'', \omega) n_{1\sigma''}(r'', \omega) \right\} \quad (119)$$

The exact excitation energies Ω_n are given by the poles of the density-density response function, and the density response diverges if the system is subject to any perturbation at precisely such a frequency. In fact, an external perturbation is not even required: a system can sustain a finite response at its excitation frequencies without any external stimulation. This finite response has the character of an eigenmode of the system. In order to calculate the eigenmodes and eigenfrequencies we start from the linear-response equation without an external perturbation v_1

$$n_{1\sigma}(r, \Omega) = \sum_{\sigma' \sigma''} \int dr' \chi_{s, \sigma \sigma'}(r, r', \Omega) \int dr'' f_{Hxc, \sigma' \sigma''}(r', r'', \Omega) n_{1\sigma''}(r'', \Omega). \quad (120)$$

This equation is an eigenvalue equation of a frequency-dependent integral operator acting on $n_{1\sigma}(r, \omega)$, and the frequencies Ω which give the eigenvalue 1 are the excitation energies we are looking for. This eigen value equation can be written in the following compact matrix notation known as

Casida equation

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Omega \begin{pmatrix} -I & 0 \\ 0 & I \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (121)$$

(ME Casida, In "Recent Advances in Density Functional Methods", pp 155-192 (World Scientific, Singapore 1995); R Bauernschmitt, R Ahlrichs, Chem Phys Lett **256**, 454 (1996).)

Here the matrix elements of A and B are given by

$$A_{ia\sigma, i'a'\sigma'}(\Omega) = \delta_{ii'} \delta_{aa'} \delta_{\sigma\sigma'} \omega_{a'i'\sigma'} + \underbrace{\int dr \int dr' \varphi_{i\sigma}^{0*}(r) \varphi_{a\sigma}^0(r) f_{Hxc, \sigma\sigma'}(r, r', \Omega) \varphi_{i'\sigma'}^0(r') \varphi_{a'\sigma'}^{0*}(r')}_{K_{ia\sigma, i'a'\sigma'}(\Omega)} \quad (122)$$

$$B_{ia\sigma, i'a'\sigma'}(\Omega) = K_{ia\sigma, i'a'\sigma'}(\Omega) \quad (123)$$

and

$$X_{ia\sigma}(\Omega) = - \left\{ \sum_{\sigma'} \sum_{jk} \frac{f_{j\sigma} - f_{k\sigma}}{\Omega - \omega_{jk\sigma'}} \int dr \int dr' \varphi_{i\sigma}^{0*}(r) \varphi_{a\sigma}^0(r) f_{Hxc, \sigma\sigma'}(r, r', \Omega) \varphi_{j\sigma'}^0(r') \varphi_{k\sigma'}^{0*}(r') \right\} \frac{1}{\Omega - \omega_{ia\sigma}} \quad (124)$$

$$Y_{ia\sigma}(\Omega) = -X_{ai\sigma}(\Omega) \quad (125)$$

while I is the identity matrix.

The Casida equation yields, in principle, the exact excitation energies Ω_n of any many-body system, under the following conditions:

- The exact Kohn-Sham ground state of the system must be calculated, which requires knowledge of the exact $v_{xc}^0[n_0]$. All occupied and unoccupied Kohn-Sham orbitals and energy eigen value $\varphi_{j\sigma}^0(r)$ and $\epsilon_{j\sigma}$ are needed, including the continuum states.
- The exact frequency-dependent xc Kernel $f_{xc,\sigma\sigma'}[n_0](r, r', \omega)$ is required.
- The infinite-dimensional pseudo-eigenvalue equation has to be solved. Since the elements of the matrices A and B depend on the frequency via $f_{xc,\sigma\sigma'}$, this requires not just one diagonalization, but some sort of an iterative scheme.

In practice, none of these requirements can be satisfied exactly, only to varying degrees of approximation.

If we set the coupling-matrix elements $K_{ia\sigma,i'a'\sigma'}$ to zero, the Casida equation simply reproduces the Kohn-Sham excitation energies $\omega_{ia\sigma}$ as eigenvalues.

In practice, the Casida equation is often cast into the alternative form

$$CZ = \Omega^2 Z. \quad (126)$$

To arrive at this expression, one assumes that the Kohn-Sham orbitals are real and that f_{xc} is frequency-independent, so that the matrices A and B become real. Then it holds

$$C = (A - B)^{\frac{1}{2}}(A + B)(A - B)^{\frac{1}{2}} \quad (127)$$

$$Z = (A - B)^{\frac{1}{2}}(X - Y) \quad (128)$$

Using the explicit forms of the matrix elements of A and B one finds

$$\sum_{i'a'\sigma'} [\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}\omega_{a'i'\sigma'}^2 + 2\sqrt{\omega_{ai\sigma}\omega_{a'i'\sigma'}}K_{ia\sigma,i'a'\sigma'}]Z_{i'a'\sigma'} = \Omega^2 Z_{ia\sigma} \quad (129)$$

This approximate version of the Casida equation is implemented in most TDDFT codes.

5.5. The Tamm-Dancoff approximation

The eigenvalues of the Casida equation in the form

$$CZ = \Omega^2 Z \quad (130)$$

are the squares of the excitation energies; this means that for each excitation energy Ω_n the Casida formalism also delivers the corresponding negative value, $-\Omega_n$. The excitation energies thus come in pairs, which is also evident from the pole structure of the response function (cf. Appendix A). Physically, the pair $(\Omega_n, -\Omega_n)$ corresponds to the excitations and deexcitations of the system. The approximation to the exact TDDFT linear-response scheme in which all deexcitation processes are neglected is called the **Tamm-Dancoff approximation** (TDA). Technically, one simply sets the off-diagonal matrices B in the Casida equations to zero, but keeps the matrix A as it is. This results in the simpler eigen value problem

$$AX = \Omega X \quad (131)$$

The coupling matrix elements $K_{ia\sigma, i'a'\sigma'}$ decay relatively rapidly away from the diagonal, because the overlap of increasingly different orbitals becomes smaller by cancellation of oscillations. By ignoring all off-diagonal elements of the matrices A and B in the Casida equation one arrives at the so-called **small-matrix approximation** (SMA)

$$\Omega_{\pm}^2 = \omega_{ia\sigma}^2 + 2\omega_{ia\sigma}[K_{ia\sigma, ia\sigma}(\Omega) \pm K_{ia\sigma, ia\bar{\sigma}}(\Omega)] \quad (132)$$

where $\bar{\sigma}$ denotes the opposite of the spin σ and Ω_{\pm} corresponds to the singlet / triplet excitation energies. The SMA can be simplified further by making the TDA, i.e., by including only the positive excitation energy, which leads to

$$\Omega_{\pm} = \omega_{ia\sigma} + [K_{ia\sigma, ia\sigma}(\Omega) \pm K_{ia\sigma, ia\bar{\sigma}}(\Omega)] \quad (133)$$

If furthermore the frequency-dependence of the xc Kernel is neglected, one arrives at the **single-pole approximation** (SPA)

$$\Omega_{\pm} = \omega_{ia\sigma} + [K_{ia\sigma, ia\sigma}(\omega_{ia\sigma}) \pm K_{ia\sigma, ia\bar{\sigma}}(\omega_{ia\bar{\sigma}})] \quad (134)$$

Assuming that the Kohn-Sham ground state is not spin-polarized, so that $\omega_{ia\uparrow} = \omega_{ia\downarrow} = \omega_{ia}$ the SPA has the following two solutions

$$\Omega_+ = \omega_{ia} + 2 \int dr \int dr' \varphi_i^{0*}(r) \varphi_a^0(r) \left[\frac{1}{|r-r'|} + f_{xc}(r, r', \omega_{ia}) \right] \varphi_i^0(r') \varphi_a^0(r') \quad (135)$$

$$\Omega_- = \omega_{ia} + 2 \int dr \int dr' \varphi_i^{0*}(r) \varphi_a^0(r) g_{xc}(r, r', \omega_{ia}) \varphi_i^0(r') \varphi_a^0(r') \quad (136)$$

where

$$f_{xc}(r, r', \omega) = \frac{1}{2}[f_{xc\uparrow\uparrow}(r, r', \omega) + f_{xc\uparrow\downarrow}(r, r', \omega)] \quad (137)$$

and

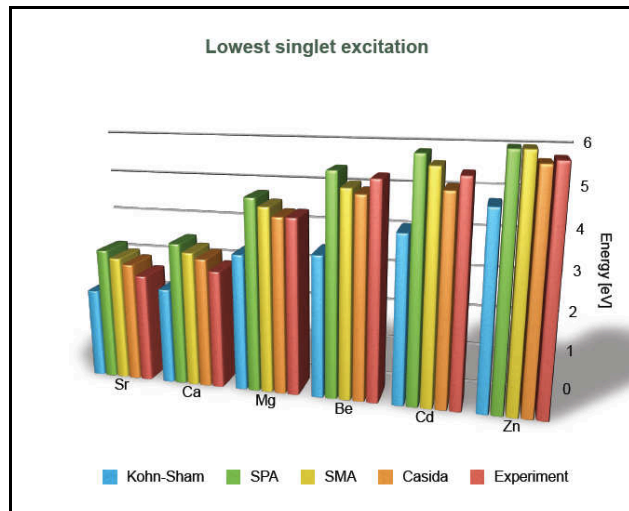
$$g_{xc}(r, r', \omega) = \frac{1}{2}[f_{xc\uparrow\uparrow}(r, r', \omega) - f_{xc\uparrow\downarrow}(r, r', \omega)] \quad (138)$$

$f_{xc\uparrow\uparrow}$ and $f_{xc\uparrow\downarrow}$ are spin-dependent xc Kernels defined in 5.4.

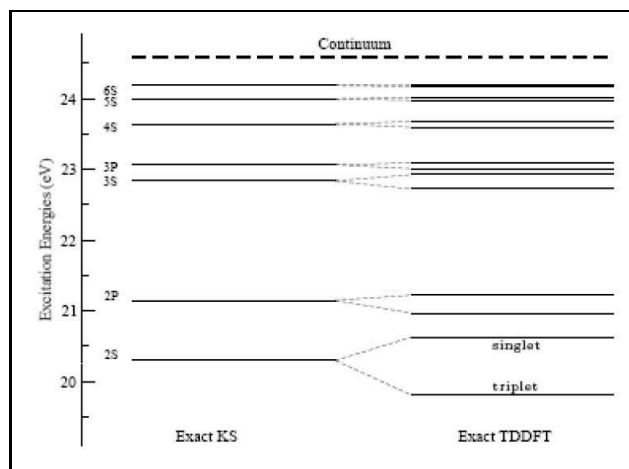
5.6. Applications of TDDFT

Today, the vast majority of applications of TDDFT are in the linear-response regime, with the general objective of describing excited-state properties of a wide variety of systems. This has made a large impact in the area of theoretical chemistry, where TDDFT methods are unrivaled when it comes to treating medium-sized and large molecules. How accurate are TDDFT results?

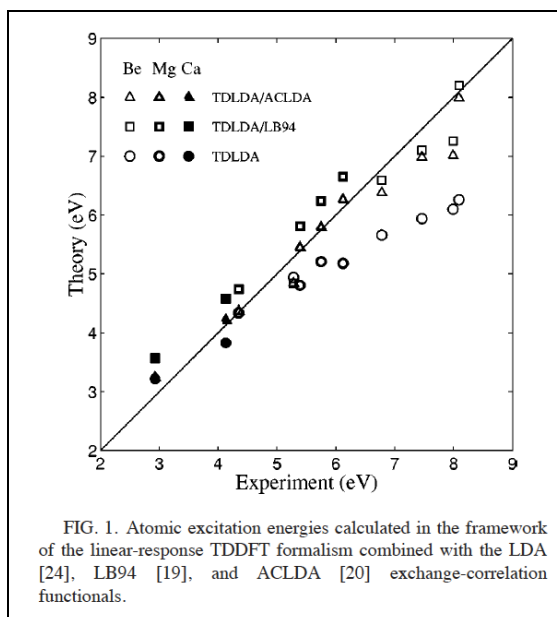
The figure below shows the lowest singlet $1S \rightarrow 1P$ excitation energies of various closed-shell atoms [Vasiliev et al., Phys. Rev. Lett. 82, 1919 (1999)], comparing the bare LDA Kohn-Sham excitations, TDDFT excitation energies, and experimental values. The TDDFT excitation energies were calculated within the ALDA, using the full Casida approach, the SMA, and the SPA. The bare LDA Kohn-Sham excitations are found to be significantly too low, with errors ranging from around 0.5 eV (Ca and Sr) to 1.78 eV (Be). This is a very typical observation, and is related to the wrong asymptotic behavior of the LDA (and most other semilocal xc potentials). The full Casida formalism of TDDFT gives a much better agreement with experiment, with a maximum deviation of not more than around 0.3 eV. The simplified TDDFT approaches are seen to somewhat overcorrect: The SMA gives excitation energies that are typically around 0.4 - 0.5 eV too high, and the SPA overshoots a little more. But the bottom line is that even the simplest TDDFT correction to the bare Kohn-Sham excitation energies gives a significant improvement, often reducing the error by half.



For atomic He it is possible to construct the exact KS potential and the exact TDDFT potential, hence compare the one electron eigenvalues of the former with the predicted excitation energies of the latter. The figure below shows the excitation energies of the He atom [cf. Petersilka et al., International Journal of Quantum Chemistry, 80, 534 (2000)]. The singlet excitation is always above the bare Kohn-Sham excitation, whereas the triplet excitation is always below. This can easily be understood in the light of the excitation energies calculated within the SPA (Section 5.5). For the singlet energy Ω_+ the Hartree part gives a large positive correction, whereas f_{xc} produces a smaller negative contribution. For Ω_- there is no Hartree contribution, and the only effect comes from g_{xc} , which is negative. Strictly speaking, this argument is valid if the SPA is used for calculating the excitation energies; however, it carries over to the full calculation since the SPA gives the dominating contribution.

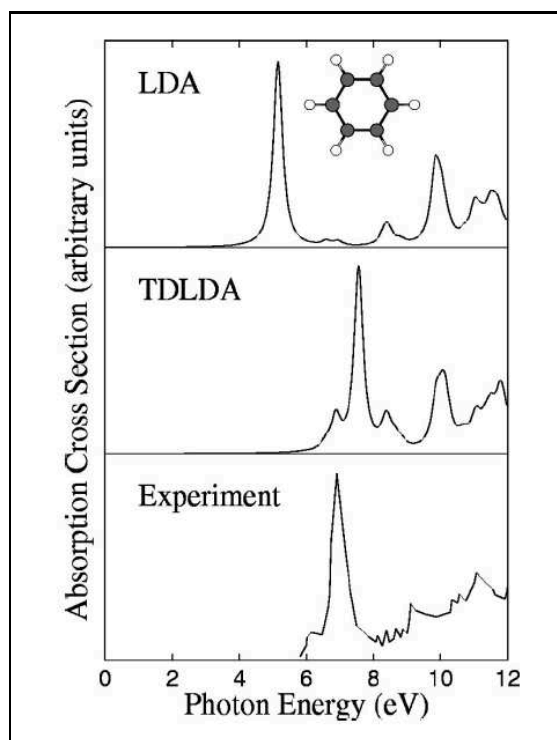


How important is the role played by xc functional used for the ground-state calculations for the excitation energies obtained within TDDFT? The figure below shows the lowest few singlet excitation energies [Vasiliev and Martin, Phys. Rev. A 69, 052508 (2004)] of Be, Mg, and Ca calculated with TDDFT within the ALDA in comparison with experiment. The ground-state calculations were done using the LDA and two xc functionals (LB94 and ACLDA) which produce the correct $-1/r$ long-range behaviour of the xc potential. Obviously, the latter produce clearly the better agreement with the experimental data.

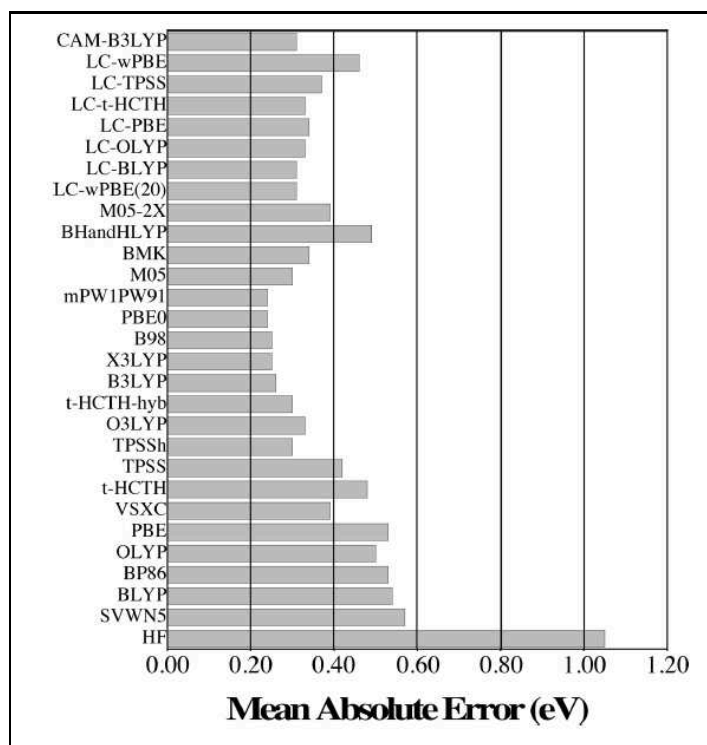


TDDFT is frequently used to calculate optical absorption spectra. As an example, we show the comparison of calculated and measured optical spectra for benzene [Vasiliev et al. Phys. Rev. B, 65, 115416 (2002)]. Here spectra are shown using the LDA Kohn-Sham excitations and the ALDA/LDA TDDFT data. Obviously, the latter agree much better with experiment than the former. However, there remain clear discrepancies with respect to line shape and excitation energies. Taking a closer look at individual excitations, one sees that the nonhybrid functionals typically underestimate the excitation energies; hybrid mixing leads to systematically higher excitation energies. The improvement is more pronounced for the singlet excitations than for triplet excitations.

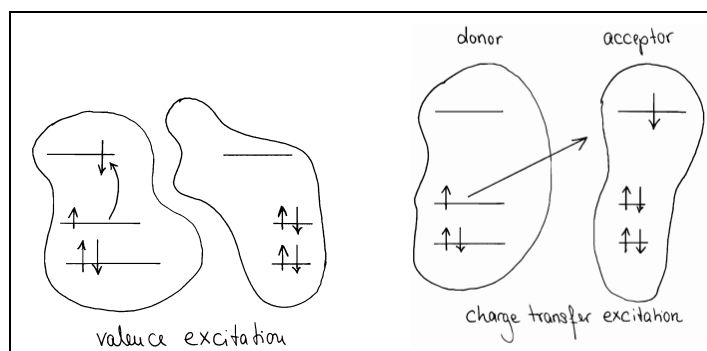
A statistically meaningful analysis of the performance of xc functionals can be carried out using test sets of molecules including a variety of organic and inorganic species. The reference data is obtained from experiment or from very accurate wave-function based theories. In the latter case, only small molecules can be included. On the other hand, experimentally determined excitation energies suffer from environmental



effects such as temperature, pressure, or solvents. This makes the comparison with theory quite challenging. The figure below shows the mean absolute error for 28 xc functionals and for the Hartree-Fock theory, obtained by calculating 103 low-lying vertical excitation energies for a test set of medium-sized organic molecules [Jacquemin et al., *J. Chem. Theory Comput.* 5, 2420 (2009)]. The Kohn-Sham ground-state calculations were performed using the same xc functionals that were used, in the adiabatic approximation, for the TDDFT calculations. No geometry optimization was performed; identical molecular geometries were used for each xc functional. We immediately see that TDHF gives very large errors (~ 1 eV), any TDDFT calculation reduces the error by at least a half. The LDA and GGAs give errors of 0.5 eV, Meta-GGAs (VSXC, TPSS) give better agreement, about 0.4 eV. For the test set considered here, the best choice is clearly given by the hybrid GGAs (B3LYP, X3LYP, B98, mPW1PW91, and PBE0), containing between 22 % and 25 % of exact exchange. In this case, the mean error is 0.25 eV. We mention that these functionals typically also lead to very accurate geometries in ground-state calculations. The long-range-corrected hybrids give a slightly larger error. However, this is also related to the specific test set, in which charge-transfer excitations are not significantly represented.



Charge-transfer excitations are processes in which charge is physically moved from one region to a second region which is spatially separated from the first, see schematic illustration below



Standard TDDFT fails in describing charge transfer excitations, i.e. excitation energies are often seriously (by several eV) underestimated.

Why is that?

Consider the case where donor and acceptor are separated by a large distance R .

In this case the minimum energy required to remove an electron from the donor is

given by the donor's ionization energy I_d . Some of that energy is regained via the acceptor's electron affinity A_a . Additionally the energy is lowered by the electrostatic interaction energy $-\frac{1}{R}$.

Altogether we obtain

$$\Omega_{ct} = I_d - A_a - \frac{1}{R} \text{ in the limit } R \rightarrow \infty \quad (139)$$

If we consider TDDFT in SPA we obtain

$$\Omega_{ct}^{SPA} = \epsilon_L^a - \epsilon_H^d + 2 \int dr \int dr' \varphi_L^a(r) \varphi_H^d(r) f_{Hxc}(r, r', \omega) \varphi_L^a(r') \varphi_H^d(r') \quad (140)$$

where L and H denote the lowest unoccupied and highest occupied orbital, respectively. $\varphi_L^a(r)$ and $\varphi_H^d(r)$ have exponentially vanishing overlap in the limit of large separation.

For all standard (semi) local, adiabatic xc kernels, TDDFT simply collapses to the difference between the bare Kohn-Sham eigen values

$$\Omega_{ct}^{SPA} \rightarrow \epsilon_L^a - \epsilon_H^d \quad (141)$$

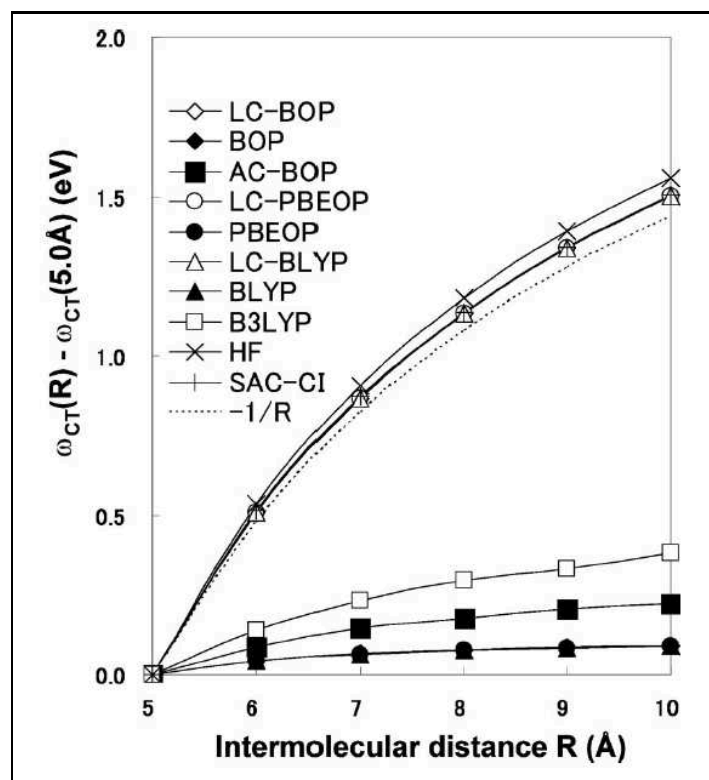
Thus, the TDDFT result is deficient in two respects. First, it misses the $\frac{1}{R}$ component of Ω_{ct} . Secondly, it suffers from the band gap underestimation of DFT

$$I_d = -\epsilon_H^d \quad (142)$$

$$A_a = -\epsilon_L^a - \Delta_{xc}^a \quad (143)$$

Here Δ_x^a is the xc correction to the Kohn-Sham gap.

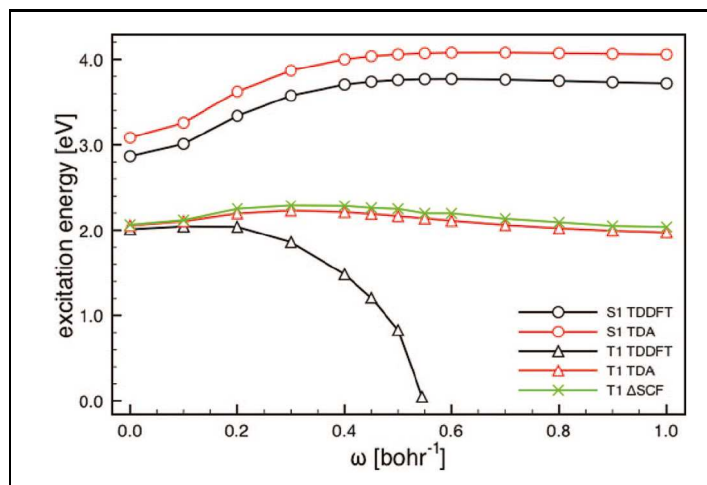
Hybrid xc functionals which contain a fraction of the exact HF exchange give some improvement over pure TDDFT methods, since they (i) lead to larger band gaps compared to DFT and (ii) result in a xc kernel for which the matrix element in the SPA does not vanish. Range-separated hybrid functionals that produce the correct asymptotic behaviour at large distances (where HF exchange takes over) and treat the short-range correlations using standard LDA or GGA often perform even better. That can be seen below [Tawada et al. J. Chem. Phys. 120, 8425 (2004)] where several hybrid functionals as well as TDHF and SAC-CI were applied to charge transfer excitations of a $C_2H_4 - C_2F_4$ dimer at varying intermolecular distances. Obviously the range-separated hybrids (here labeled LC) agree perfectly with the correct $-1/R$ behaviour, while the other functionals - regular GGA as well as hybrids - drastically underestimate the charge-transfer excitation energy of the complex. It



thus appears on the one hand as if charge-transfer excitations have now fallen into the realm of systems to be meaningfully studied by means of TDDFT.

On the other hand, while range-separated hybrids represent an increasingly popular class of functionals that have proven to be very successful for a wide range of chemical applications, the performance of these functionals for TDDFT descriptions of triplet excited states needs to be checked carefully. Triplet energies are particularly sensitive to the range-separation parameter; this sensitivity can be traced back to triplet instabilities in the ground state coming from the large effective amounts of Hartree-Fock exchange included in these functionals. As such, the use of standard long-range corrected functionals for the description of triplet states at the TDDFT level is not generally recommended. See figure below and discussion by Sears *et al.* in *J. Chem. Phys.* **135**, 151103 (2011).

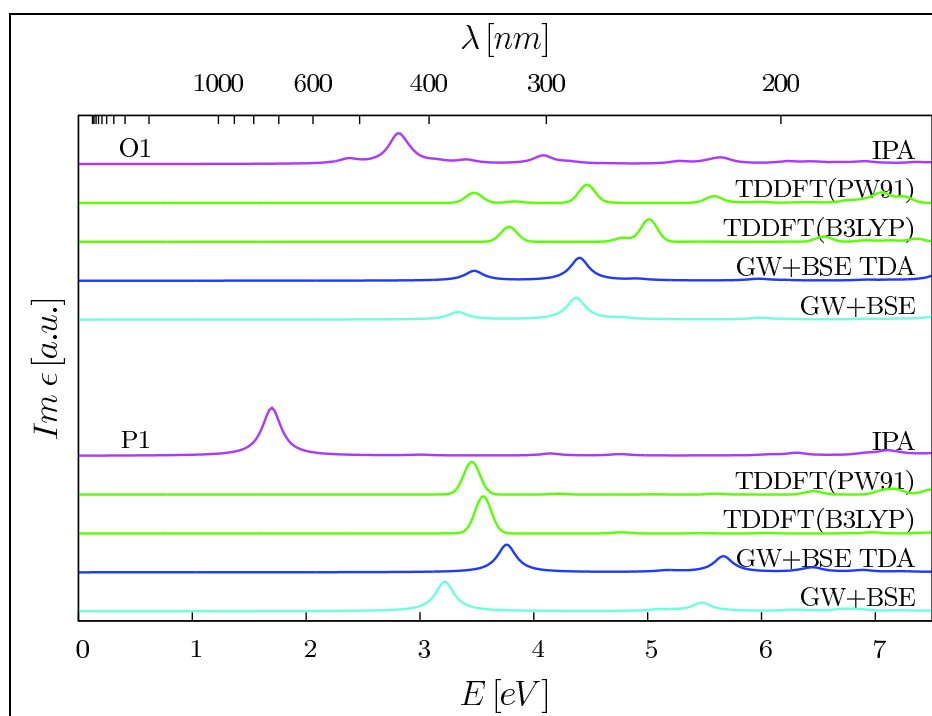
A completely different type of methods to calculate excited-state properties is referred to as propagator or Green's function approaches. At least in principle these methods are not plagued by the shortcomings of the XC functionals used within DFT. They start from the screening response of the electronic system after electronic or optical excitation. Accordingly, the dynamically screened or shielded Coulomb interaction W is the central quantity used in these methods. The excitation energies correspond to the poles of single- and two-particle Green's functions that are ob-



TDDFT and TDA-TDDFT (and Δ SCF T1) excitation energies for anthracene in a cc-pVTZ basis using the BNL functional as a function of the range-separation parameter. From Sears *et al.* in J. Chem. Phys. **135**, 151103 (2011).

tained by means of many-body perturbation theory. By evaluating the one-electron Green's function G , single-particle excitations, e.g., ionization energies and electron affinities, are derived that can be measured in photoemission and inverse photoemission spectroscopies. Two-particle Green's functions of the electronic system allow to access electron-hole pair energies and collective excitations, e.g., plasmons. In the practical implementation one resorts to approximations to describe the most relevant correlation mechanisms. Hedin's so-called GW approach, which represents a linear expansion of the XC self-energy operator Σ of the electrons in the screened potential W instead of the bare Coulomb potential (which gives only the exchange interaction), is the most widely used approximation in this context. This scheme allows for deriving a single-quasiparticle (QP) equation of a structure similar to the Kohn-Sham equation used in the DFT. Only the (semi-)local potential V^{XC} is replaced by the XC self-energy operator Σ . This suggests to calculate QP bands by using a first-order perturbative approach with respect to $(\Sigma - V^{XC})$. However, QP transition energies do in general not correctly describe optical excitation energies, i.e., photon absorption processes. The interaction of electron-hole pairs may dramatically shift the peak positions as well as appreciably distort the spectral lineshape. The electron-hole interaction is accounted for by solving the Bethe-Salpeter equation (BSE) for the polarization function [see, e.g. W.G. Schmidt *et al.* Phys. Rev. B **67**, 085307 (2003)]. Starting from DFT calculations, it has become possible to solve the BSE from first principles. Optical spectra including the effects of electron-hole interaction were obtained for a series of bulk semiconductors and insulators and their surfaces as well as molecular systems. As an example, we show below a comparison

of TDDFT results with GW+BSE calculations for a prototypical Cu_2O_2 complex, $[\text{Cu}_2(\text{en})_2\text{O}_2]^{2+}$, used to model the binuclear copper enzyme tyrosinase, from [M. Rohrmüller, S. Herres-Pawlis, M. Witte, W. G. Schmidt, J. Comput. Chem. **34**, 1035 (2013)].



Calculated optical response of the oxo (O1) and peroxo (P1) configuration of $[\text{Cu}_2(\text{en})_2\text{O}_2]^{2+}$ calculated with the independent-particle approximation (IPA, i.e., the DFT), TDDFT and the GW+BSE approach. From M. Rohrmüller, S. Herres-Pawlis, M. Witte, W. G. Schmidt, J. Comput. Chem. **34**, 1035 (2013).

6. Electron Correlation Methods

HF generates solutions to the SE where the real $e^- - e^-$ interaction is replaced by an average interaction (cf. Chapter (3.3)). In a sufficiently large basis, the HF wave function accounts for $\sim 99\%$ of the total energy, but the remaining $\sim 1\%$ is often very important for describing chemical phenomena.

HF determines the best one-determinant trial wave function (within the given basis set)

\Rightarrow In order to improve on HF results, the starting point must be a trial wave function which contains more than one Slater Determinant (SD) Ψ . This also means that the mental picture of electrons residing in orbitals has to be abandoned.

As HF solution usually gives $\sim 99\%$ of the correct answer, electron correlation methods normally use the HF wave function as a starting point for improvements.

A generic multi-determinant trial wave function can be written as

$$\Psi = a_0 \Psi^{HF} + \sum_{i=1} a_i \Psi_i$$

with $a_0 \approx 1$.

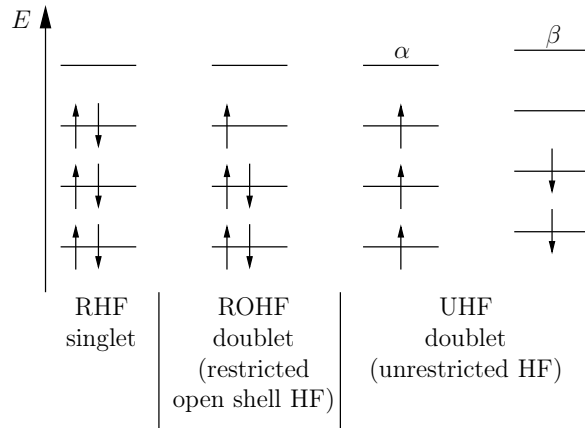
How are the additional determinants beyond HF constructed?

$$\left. \begin{array}{l} N \text{ electrons} \\ M \text{ molecular orbitals (MOs)} \end{array} \right\} \begin{array}{l} \frac{N}{2} \text{ occupied MO for RHF} \\ M - \frac{N}{2} \text{ virtual (unoccupied) MOs} \end{array}$$

Remark

Not introduced yet: RHF: Restricted HF

\rightarrow each spatial orbital should have two electrons, one with α and one with β spin



back to determinants:

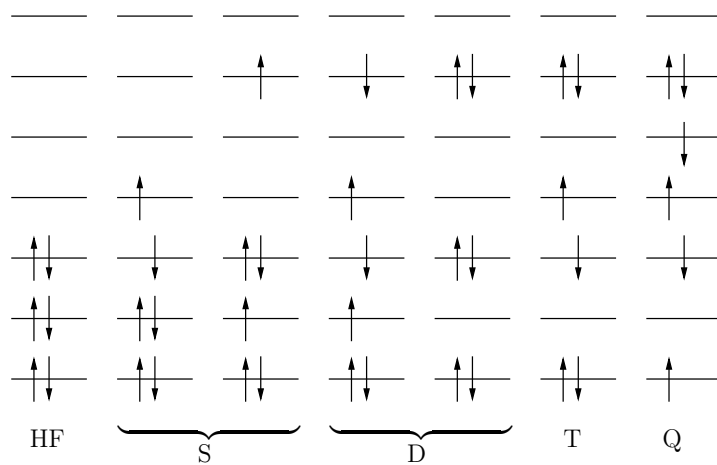
Slater determinant: $\frac{N}{2}$ spatial MO \rightarrow N spinorbitals

replace now occupied MOs by virtual MOs

\rightarrow can generate a whole series of determinants, these can be denoted according to how many occupied HF MOs have been replaced by virtual MOs, i.e., SDs which are **singly**, **doubly**, **triply**, etc. excited relative to the HF determinant, up to a maximum of N excited electrons

\rightarrow notation: Singles (S)
Doubles (D)
Triples (T)
Quadruples (Q) etc.

Example: Excited SDs generated from a HF reference



The total number of determinants that can be generated depends on the basis: more virtual MOs → more excited determinants can be constructed.

If all possible determinants in a given basis set are included, all the electron correlation (in the given basis) is (or can be) recovered! For an infinite basis the SE is then solved exactly.

Remarks

- (i) important chemical changes take place in the valence orbitals, core orbitals almost const. → limit the number of determinants to those which can be generated by exciting valence electrons...**frozen core approximation**
- (ii) sometimes also the highest virtual orbitals corresponding to the anti-bonding combinations of the core orbitals are removed from the correlation treatment → **frozen virtuals**
- (iii) notation introduced by J.A. Pople:

| | | |
|---|--|---|
| $\underbrace{\text{''level 2/basis 2''}}_{\text{electronic}}$ | | $\underbrace{\text{''level 1/basis 1''}}_{\text{geometry}}$ |
| structure calculation | | optimization |

''level'' $\hat{=}$ ''level of theory'' → how much electron correlation?

''basis'' $\hat{=}$ ''basis set''

Later we speak about basis sets, now we turn to electron correlation. There are three main methods for calculating electron correlation: **Configuration Interaction** (CI), **Many Body Perturbation Theory** (MBPT) and **Coupled Cluster** (CC)

6.1. Configuration Interaction

trial wave function

$$\Psi^{CI} = a_0 \Psi^{SCF} + \sum_S a_S \Psi_S + \sum_D a_D \Psi_D + \sum_T a_T \Psi_T + \dots$$

Ψ^{SCF} : taken from self-consistent HF calculation, MOs from HF are held fixed in the following ($= \Psi_0$)

Subscripts S, D, T, \dots → indicate determinants that are singly, doubly, triply, etc. excited relative to HF
 constraint optimization (total CI wave function is normalized)

$$L = \langle \Psi^{CI} | H | \Psi^{CI} \rangle - \lambda [\langle \Psi^{CI} | \Psi^{CI} \rangle - 1]$$

$\stackrel{!}{=} H^e$ in the following always H

$$\begin{aligned} \langle \Psi^{CI} | H | \Psi^{CI} \rangle &= \sum_{i=0} \sum_{j=0} a_i a_j \langle \Psi_i | H | \Psi_j \rangle \\ &= \sum_{i=0} a_i^2 E_i + \sum_{i=0} \sum_{j \neq i} a_i a_j \langle \Psi_i | H | \Psi_j \rangle \end{aligned}$$

$$\begin{aligned} \langle \Psi^{CI} | \Psi^{CI} \rangle &= \sum_{i=0} \sum_{j=0} a_i a_j \langle \Psi_i | \Psi_j \rangle \\ &= \sum_{i=0} a_i^2 \langle \Psi_i | \Psi_i \rangle = \sum_{i=0} a_i^2 \end{aligned}$$

(The overlap elements between different determinants are zero, as they are built from orthogonal MOs)

$$\begin{aligned} \frac{\partial L}{\partial a_i} &\stackrel{!}{=} 0 \\ \Rightarrow a_i(E_i - \lambda) + \sum_{j \neq i} a_j \langle \Psi_i | H | \Psi_j \rangle &= 0 \end{aligned}$$

one such equation for each a_i

→ matrix notation: $\lambda = E$, $\langle \Psi_i | H | \Psi_j \rangle = H_{ij}$

$$\begin{pmatrix} H_{00} - E & H_{01} & \dots & H_{0j} & \dots \\ H_{10} & H_{11} - E & \dots & H_{1j} & \dots \\ \vdots & \vdots & & \vdots & \vdots \\ H_{j0} & \dots & \dots & H_{jj} - E & \dots \\ \vdots & \dots & \dots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ \vdots \\ a_j \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ \vdots \end{pmatrix}$$

shorthand $(H - EI)a = 0 \iff Ha = Ea$

⇒ need to diagonalize the CI matrix, eigenvector contains the a_i coefficients in front of the determinants

eigenvalues → ground- and excited state energies

$H = H^e$: sum of one-electron and two-electron operators

⇒ if two determinants differ by more than two spatial MOs then matrix element with H will be zero

⇒ CI matrix acquires a block diagonal structure

| | Ψ^{HF} | Ψ_S | Ψ_D | Ψ_T | Ψ_Q | ... |
|-------------|--------------|--------------|----------|----------|----------|-----|
| Ψ^{HF} | E^{HF} | $\mathbf{0}$ | \times | 0 | 0 | 0 |
| Ψ_S | $\mathbf{0}$ | \times | \times | \times | 0 | 0 |
| Ψ_D | \times | \times | \times | \times | \times | 0 |
| Ψ_T | 0 | \times | \times | \times | \times | |
| Ψ_Q | 0 | 0 | \times | \times | \times | |
| \vdots | 0 | 0 | 0 | | | |

Brillouin's theorem: disappearance of matrix elements between the HF reference and singly excited states
[L. Brillouin, Actualities Sci. Ind. 71, 159 (1934)]

Question: Size of CI matrix?

Example: H_2O with 10 electrons and 38 spin-MO (10 occupied, 28 empty)

⇒ $\frac{38!}{10!(38-10)!}$ possibilities to excite electrons into virtual orbitals

⇒ number of excited determinants grows factorially with the size of the basis set

- ▶ Many of these excited determinants have different spin multiplicity and can therefore be left out if we are searching for the singlet ground state
- ▶ Employ symmetry (C_{2v}) of the molecule

⇒ dimension of CI matrix: 30 046 752

⇒ need to diagonalize a $30 \cdot 10^6 \times 30 \cdot 10^6$ matrix, clearly impossible

→ Can, however, use iterative algorithms to calculate the lowest (or a few of the lowest) eigenvalue(s) and -vector(s)

→ most commonly used: Davidson algorithm *[E. Davidson, I. Comput. Phys. 17, 87 (1975)]*

Still, full CI calculations are not a routine comp. procedure, rather used as a reference.

Must reduce number of excited determinants
 → computationally tractable models

CIS: CI with Singles, truncating the excitation level at 1
 matrix elements $\langle \Psi^{HF} | H | \Psi_S \rangle = 0$

⇒ $\text{CIS} \hat{=} \text{HF}$ for ground state energies (because of Brillouin's theorem there are no non-vanishing matrix elements between $|\Psi^{HF}\rangle$ and $|\Psi_S\rangle$), better approximation to excited state energies, however, compared to HF

CID: CI with Doubles

Compared to the number of Doubles there are relatively few Singles ⇒ makes sense to include both →

$$\left. \begin{array}{l} \text{CISD} \quad \sim O(M^6) \\ \text{CISDT} \quad \sim O(M^8) \\ \text{CISDTQ} \quad \sim O(M^{10}) \end{array} \right\} \begin{array}{l} M: \# \text{ basis functions} \\ \text{CPU scaling} \end{array}$$

CISDTQ gives in general results close to full CI, however, it can only be applied to very small molecules. The only CI method which is generally applicable for a large variety of systems is CISD. It recovers typically 80-90% of the correlation energy.

Examples:

- (i) **full CI for Ne atom** in $[5s, 4p, 3d]$ basis (cf. chapter 7 for notation) where 1s electrons are excluded from correlation

$$\Psi^{CI} = \sum_{i=0} a_i \Psi_i$$

[J. Olsen et al. *Chem. Phys. Lett.* **169**, 463 (1990)]

| i | $ a_i ^2$ |
|-----|-------------------|
| 0 | 0.9644 |
| 1 | 0.0010 |
| 2 | 0.0337 |
| 3 | 0.0004 |
| 4 | 0.0005 |
| 5 | $1 \cdot 10^{-5}$ |
| 6 | $1 \cdot 10^{-6}$ |
| 7 | $1 \cdot 10^{-7}$ |
| 8 | $1 \cdot 10^{-9}$ |

⇒ double excited determinants are by far the most important
 Why? Because only doubly excited determinants have non-zero matrix elements with the HF ground state!

(ii) H_2 molecule with minimum basis, i.e., one s -function on each centre, χ_A and χ_B .

RHF \rightarrow 2 MOs, ϕ_1 and ϕ_2

$$\begin{aligned}\phi_1 &= N_1(\chi_A + \chi_B) : && \text{bonding MO} \\ \phi_2 &= N_2(\chi_A - \chi_B) : && \text{antibonding MO}\end{aligned}$$

$$\Psi_0 = \begin{bmatrix} \phi_1(1) & \bar{\phi}_1(1) \\ \phi_1(2) & \bar{\phi}_1(2) \end{bmatrix} \leftarrow \begin{array}{l} \text{HF wave function} \\ \text{two electrons in the lowest (bonding) MO} \end{array}$$

N_1, N_2 : normalization constants

$$\begin{aligned}\phi_1 &= \phi_1\alpha && (\text{Spin up}) \\ \bar{\phi}_1 &= \phi_1\beta && (\text{Spin down})\end{aligned}$$

form excited SD available in this basis:

$$\begin{array}{l} \Psi_1 = \begin{bmatrix} \phi_2(1) & \bar{\phi}_2(1) \\ \phi_2(2) & \bar{\phi}_2(2) \end{bmatrix} \rightarrow \text{Double} \\ \Psi_2 = \begin{bmatrix} \phi_1(1) & \bar{\phi}_2(1) \\ \phi_1(2) & \bar{\phi}_2(2) \end{bmatrix} \\ \Psi_3 = \begin{bmatrix} \bar{\phi}_1(1) & \phi_2(1) \\ \bar{\phi}_1(2) & \phi_2(2) \end{bmatrix} \\ \Psi_4 = \begin{bmatrix} \phi_1(1) & \phi_2(2) \\ \phi_1(2) & \phi_2(2) \end{bmatrix} \\ \Psi_5 = \begin{bmatrix} \bar{\phi}_1(1) & \bar{\phi}_2(1) \\ \bar{\phi}_1(2) & \bar{\phi}_2(2) \end{bmatrix} \end{array} \left. \vphantom{\begin{array}{l} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{array}} \right\} \begin{array}{l} \rightarrow \text{Singles} \\ S_z = 1 \\ S_z = -1 \end{array}$$

H_2 molecule has $D_{\infty h}$ symmetry

\Rightarrow full CI for \sum_g^1 states only involves two configurations: Ψ_0 and Ψ_1

$$\begin{aligned}\Psi_0 &= \phi_1(1)\bar{\phi}_1(2) - \bar{\phi}_1(1)\phi_1(2) =: \phi_1\phi_1(\alpha\beta - \beta\alpha) \\ \Psi_1 &= \phi_2(1)\bar{\phi}_2(2) - \bar{\phi}_2(1)\phi_2(2) =: \phi_2\phi_2(\alpha\beta - \beta\alpha)\end{aligned}$$

Ignoring the spin functions (can be integrated out since H is spin independent) and the normalization we can expand into AOs

$$\begin{aligned}\Psi_0 &= (\chi_A(1) + \chi_B(1))(\chi_A(2) + \chi_B(2)) \\ &=: \chi_A\chi_A + \chi_B\chi_B + \chi_A\chi_B + \chi_B\chi_A \\ \Psi_1 &= (\chi_A(1) - \chi_B(1))(\chi_A(2) - \chi_B(2)) \\ &=: \underbrace{\chi_A\chi_A + \chi_B\chi_B}_{\substack{\text{both electrons on the same} \\ \text{centre, ionic contributions to} \\ \text{the wave function, } H^+H^-}} - \underbrace{\chi_A\chi_B - \chi_B\chi_A}_{\substack{\text{covalent contributions} \\ \text{to the wave function,} \\ H^\bullet H^\bullet}}\end{aligned}$$

$$\begin{aligned}\Psi^{CI} &= a_0\Psi_0 + a_1\Psi_1 \\ &= (a_0 + a_1)(\chi_A\chi_A + \chi_B\chi_B) \\ &\quad + (a_0 - a_1)(\chi_A\chi_B + \chi_B\chi_A)\end{aligned}$$

variational procedure \rightarrow optimum values for a_0 and a_1

HF \rightarrow constrains both electrons to move in the same bonding orbital

$a_1 \neq 0 \rightarrow$ electrons can avoid each other better, because the antibonding MO becomes available, this has a nodal plane (where $\phi_2 = 0$) and the electrons may be on opposite sides of this plane

thought experiment: increase the distance between the atoms $R \rightarrow \infty$

independent from R , HF wave function is always an equal mixture of ionic and covalent terms

$\rightarrow H_2 \rightarrow 50\%H^+H^- + 50\%H^\bullet H^\bullet$

this may lead to problems

Example: bonds dissociate homolytically, i.e., ionic contribution should be zero

\Rightarrow HF dissociation energy is far higher than the experiment

- \rightarrow (i) too high activation energies in RHF
- (ii) equilibrium bond lengths too short
- (iii) vibrational energies too high
- (iv) wave function too "ionic" \rightarrow dipole moment and atomic charges too large

Dissociation problem can be solved by CI

$a_1 = -a_0 \rightarrow$ ionic term disappears

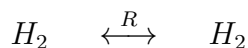
For a given distance R we can calculate the optimum ratio between a_1 and a_0 and can thus correctly model the dissociation with CI.

Size Consistency?

full CI impossible, except for trivial systems

\rightarrow need to truncate, consider for example CISD

calculate total energy of two H_2 molecules as a function of distance R



within CISD we may have

- ▶ single excitation on either H_2
- ▶ single excitations on both H_2
- ▶ double excitations on either H_2

irrespective of R , if $R \rightarrow \infty$ we can perform the calculations for a single H_2 molecule, may have

- ▶ single excitations
- ▶ double excitation

The latter, however, corresponds to a quadruply excited H_4 system

$$\Rightarrow 2E^{CISD}(H_2) < E^{CISD}(H_2 + H_2)!$$

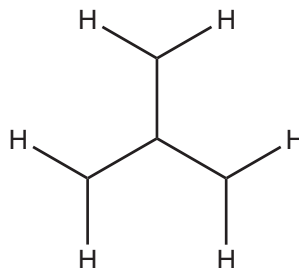
Full CI is size consistent, but all forms of truncated CI are not! CISD recovers less and less electron correlation as the system grows larger.

Multi-configuration Self-consistent Field (MCSCF)

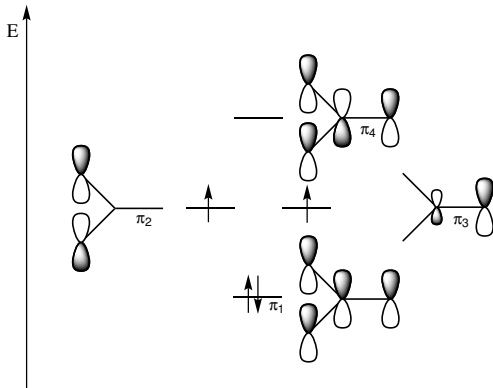
is CI, where **not only the coefficients** in front of the determinants **are optimized** by the variational principle, **but also the MOs** that are used for constructing the determinants.

Example: TMM (trimethylenemethane)

22 valence electrons
9 σ bonds



\Rightarrow 4 electrons for 4π orbitals, ground state is triplet (cf. figure below):



can start RHF calculation with either

$$\Psi = |\dots \pi_1^2 \pi_2^2 \pi_3^0 \rangle \quad \text{or}$$

$$\Psi_{\pi_2 \rightarrow \pi_3} = |\dots \pi_1^2 \pi_2^0 \pi_3^2 \rangle$$

where the MOs have been kept constant. We could also start with a wave function, where the π_3 orbital has been populated from the beginning

$$\Psi' = |\dots \pi_1'^2 \pi_2'^0 \pi_3'^2 \rangle$$

Now the π' orbitals are adapted to the $\pi_2 \rightarrow \pi_3$ excitation

$$\Rightarrow E(\Psi') < E(\Psi_{\pi_2 \rightarrow \pi_3})$$

From the nature of the problem, however, we would really like π_2 and π_3 to be treated equivalently

→ minimize energy of the two-configuration wave function

$$\Psi_{MCSCF} = a_1 |\dots \pi_1^2 \pi_2^2 \rangle + a_2 |\dots \pi_1^2 \pi_3^2 \rangle$$

→ orbitals are optimized for a combination of configurations

Remarks

- ▶ nature of the SCF process

→ root of the problem:

Only occupied orbitals contribute to the electronic energy - virtual orbitals do not. Therefore no driving force to optimize the shapes of virtual orbitals, they are only required to be orthogonal to the occupied MOs. Therefore the quality of the shape of the orbital π_3 in the example above depends on whether it is determined as an occupied or a virtual orbital

- ▶ static vs. dynamic correlation:
for chemists the **static correlation** is the energy gained upon allowing the orbitals (e.g. π_3 above) to relax. The remaining energy lowering by correlating the motion of the electrons is the **dynamic correlation**.
 → MCSCF methods are mainly used for generating the "static" part of the correlation

Complete Active Space Self-consistent Field (CASSCF)

(also called Full Optimized Reaction Space (FORS))

- ▶ partition the MOs into active and inactive spaces
- ▶ active space: typically some of the highest occupied and some of the lowest unoccupied MOs from an RHF calculation
- ▶ inactive space: MOs have either 2 or 0 electrons
- ▶ within the active MOs → full CI
 all symmetry adapted configurations → MCSCF optimization
 Which MOs to include depends on the problem: the active space should include all orbitals that change significantly for the chemical reaction of interest.
- ▶ notation $[n, m]$ -CASSCF
 → n electrons distributed in all possible ways in m orbitals
 CASSCF computationally very expensive →

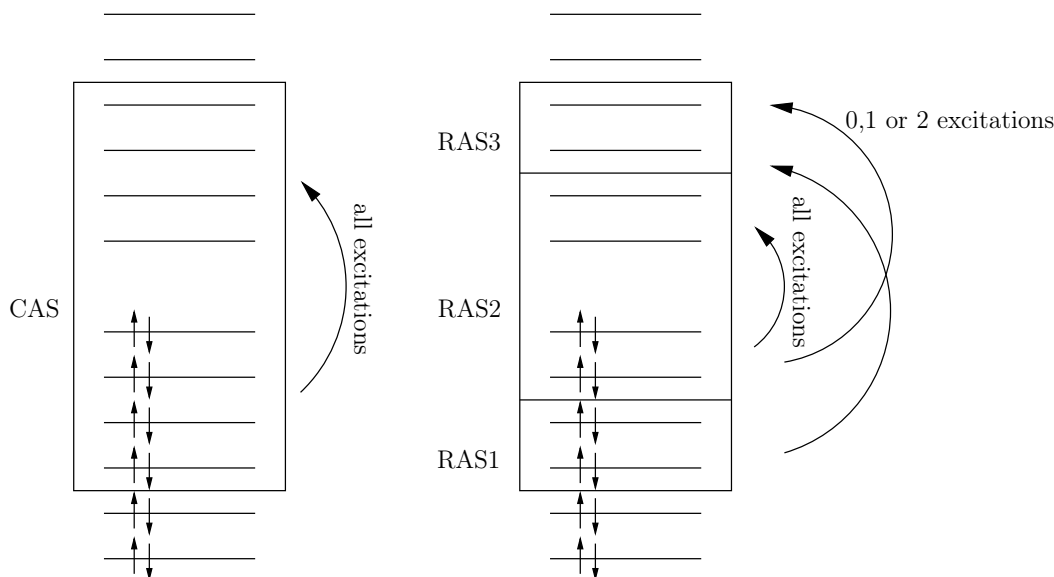
Restricted Active Space Self-consistent Field (RASSCF)

active MOs are further divided into three sections (see figure below):

- ▶ RAS1: MOs which are doubly occupied in the reference determinant
- ▶ RAS2: both occupied and unoccupied orbitals
- ▶ RAS3: MOs which are empty in the reference

Configurations in the RAS2 are generated by a full CI, analogous to CASSCF, and additional configurations are generated by allowing for a maximum of two electrons (for example) to be excited from the RAS1 and a maximum of two electrons to be excited to the RAS3

$$\Rightarrow \text{RASSCF} = \text{full CI in RAS2} + \text{CISD in RAS1 \& RAS3}$$



Number of configurations in a $[n, n]$ CASSCF wave function:

| n | 2 | 4 | 6 | 8 | 10 | 12 |
|-----|---|----|-----|------|-------|--------|
| # | 3 | 20 | 175 | 1764 | 19404 | 226512 |

→ for practical calculations one is limited to about 10-12 electrons/MOs in the active space

→ "correct" choice of active space very important

⇒ MCSCF methods are not "black box" methods like HF or DFT, need prior knowledge about the chemistry of the problem at hand! (For example from a simple calculation.)

6.2. Many-body Perturbation Theory

Short reminder:

$H = H_0 + \lambda H'$ H_0 : reference Hamiltonian

H' : perturbation

λ : strength of perturbation

SE for H_0 is solved:

$$H_0 \Phi_i = E_i \Phi_i, \quad i = 0, 1, 2, \dots, \infty$$

H_0 hermitian $\rightarrow \{\Phi_i\}$ complete set, can be chosen to be orthonormal

perturbed SE, consider non-degenerate ground state $H\Psi = W\Psi$
with

$$\begin{aligned} W &= \lambda^0 W_0 + \lambda^1 W_1 + \lambda^2 W_2 + \lambda^3 W_3 + \dots \\ \Psi &= \lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \dots \\ &\text{(Taylor expansion in } \lambda) \end{aligned}$$

$$\lambda = 0 \Rightarrow \Psi_0 = \Phi_0, \quad W_0 = E_0$$

chose perturbed wave function to be intermediately normalized, i.e.

$$\langle \Psi | \Phi_0 \rangle = 1$$

$$\begin{aligned} \Rightarrow \quad &\langle \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots | \Phi_0 \rangle = 1 \\ &\underbrace{\langle \Psi_0 | \Phi_0 \rangle}_{=1} + \lambda_1 \langle \Psi_1 | \Phi_0 \rangle + \dots = 1 \\ \Rightarrow &\langle \Psi_{i \neq 0} | \Phi_0 \rangle = 0 \end{aligned}$$

Taylor expansion in SE

$$\begin{aligned} (H_0 + \lambda H')(\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \dots) &= \\ (\lambda^0 W_0 + \lambda^1 W_1 + \lambda^2 W_2 + \dots)(\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \dots) & \end{aligned}$$

holds for any value of λ , collect terms with the same power of λ

$$\begin{aligned} \lambda^0 : H_0 \Psi_0 &= W_0 \Psi_0 \\ \lambda^1 : H_0 \Psi_1 + H' \Psi_0 &= W_0 \Psi_1 + W_1 \Psi_0 \\ \lambda^2 : H_0 \Psi_2 + H' \Psi_1 &= W_0 \Psi_2 + W_1 \Psi_1 + W_2 \Psi_0 \\ &\vdots \\ \lambda^n : H_0 \Psi_n + H' \Psi_{n-1} &= \sum_{i=0}^n W_i \Psi_{n-1} \end{aligned}$$

consider λ^1 term, apply $\int \Psi_0(r) d^3r$

$$\begin{aligned} \Rightarrow \quad &\langle \Psi_0 | H_0 \Psi_1 \rangle + \langle \Psi_0 | H' \Psi_0 \rangle = W_0 \langle \Psi_0 | \Psi_1 \rangle \\ &\quad \quad \quad + W_1 \langle \Psi_0 | \Psi_0 \rangle \end{aligned}$$

$$W_0 \underbrace{\langle \Psi_1 | \Psi_0 \rangle}_{=0}^* + \langle \Psi_0 | H' \Psi_0 \rangle = W_1$$

$$\Rightarrow \quad \boxed{W_1 = \langle \Psi_0 | H' \Psi_0 \rangle}$$

→ First-order correction to the energy is an average of the perturbation operator over the unperturbed wave function

First-order correction to the wave function?

expand Ψ_1 in the solutions Φ_i of the unperturbed SE

$$\Psi_1 = \sum_i c_i \Phi_i$$

λ^1 term reads now

$$H_0 \sum_i c_i \Phi_i + H' \Phi_0 = W_0 \sum_i c_i \Phi_i + W_1 \Phi_0$$

apply $\int \Phi_{j \neq 0}(r) d^3r$

$$\begin{aligned} \sum_i c_i \langle \Phi_j | H_0 \Phi_i \rangle - W_0 \sum_i c_i \langle \Phi_j | \Phi_i \rangle \\ + \langle \Phi_j | H' \Phi_0 \rangle - W_1 \langle \Phi_j | \Phi_0 \rangle = 0 \end{aligned}$$

$$\sum_i c_i E_i \langle \Phi_j | \Phi_i \rangle - c_j E_0 + \langle \Phi_j | H' \Phi_0 \rangle = 0$$

$$c_j E_j - c_j E_0 + \langle \Phi_j | H' \Phi_0 \rangle = 0$$

$$\Rightarrow \begin{cases} c_j = \frac{\langle \Phi_j | H' \Phi_0 \rangle}{E_0 - E_j} & j \neq 0 \\ c_0 = 0 \text{ (intermediate normalization)} \end{cases}$$

Starting from the λ^2 terms, analogous formulas can be generated for the second-order corrections:

Expansion $\Psi_2 = \sum_i d_i \phi_i$ leads to

$$\begin{aligned} W_2 = \sum_i c_i \langle \Phi_0 | H' \Phi_i \rangle = \sum_{i \neq 0} \frac{\langle \Phi_0 | H' \Phi_i \rangle \langle \Phi_i | H' \Phi_0 \rangle}{E_0 - E_i} \\ d_j = \sum_{i \neq 0} \frac{\langle \Phi_j | H' \Phi_i \rangle \langle \Phi_i | H' \Phi_0 \rangle}{(E_0 - E_j)(E_0 - E_i)} - \frac{\langle \Phi_j | H' \Phi_0 \rangle \langle \Phi_0 | H' \Phi_0 \rangle}{(E_0 - E_j)^2} \end{aligned}$$

The formulas for higher-order corrections become increasingly complex. The main point, however, is that all corrections can be expressed in terms of matrix elements of the perturbation operator over the unperturbed wave functions, and the unperturbed energies.

So far the theory has been completely general. Now we want to apply it to problem at hand, the calculation of correlation energy.

Must divide our electron Hamiltonian into H_0 and H'

reminder from (3.3), HF equation

$$\underbrace{\left\{ -\frac{\nabla^2}{2} + v(r) + V_{Hartree}(r) + V_x^{(k)}(r) \right\}}_{h_k} \psi_k(r) = \varepsilon_k \psi_k(r)$$

$$\text{where } V_x^{(k)} \psi_k(r) = - \sum_{i=1}^N \delta_{s_i s_k} \int \frac{\psi_i^*(r') \psi_k(r') \psi_i(r)}{|r - r'|} d^3 r$$

apply $\int \psi_k^*(r) d^3 r$; \sum_k

$$\begin{aligned} \Rightarrow \sum_k \langle \psi_k | h^k \psi_k \rangle &= T_S + E_{en} + \underbrace{2E_H + 2E_x}_{2\langle V_{ee} \rangle} = \sum_k \varepsilon_k \\ &= E^{HF} + \langle V_{ee} \rangle \end{aligned}$$

where $\langle V_{ee} \rangle$: average electron-electron repulsion

C. Møller and M. S. Plesset, *Phys. Rev.* 46, 618(1934)

suggested the choice $H_0 = \sum_k h_k$

$$\Rightarrow H' = H - H_0 = \hat{V}_{ee} - 2 \langle V_{ee} \rangle$$

$$\text{with } \hat{V}_{ee} = \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|r_i - r_j|}$$

Notation: MPn n : order of perturbation expansion

$$\text{clear from above: } E(MPO) = \sum_k \varepsilon_k$$

$$\begin{aligned} E(MP1) &= W_0 + W_1 = \sum_k \varepsilon_k + \langle \Phi_0 | \hat{V}_{ee} - 2 \langle V_{ee} \rangle | \Phi_0 \rangle \\ &= \sum_k \varepsilon_k + \langle V_{ee} \rangle - 2 \langle V_{ee} \rangle \\ &= \sum_k \varepsilon_k - \langle V_{ee} \rangle = E^{HF} \end{aligned}$$

First order MP perturbation theory yields the correction for the double counting of the electron-electron repulsion at zero order \rightarrow yields the HF energy

\Rightarrow Electron correlation energy thus starts at order 2 with this choice of H_0 !

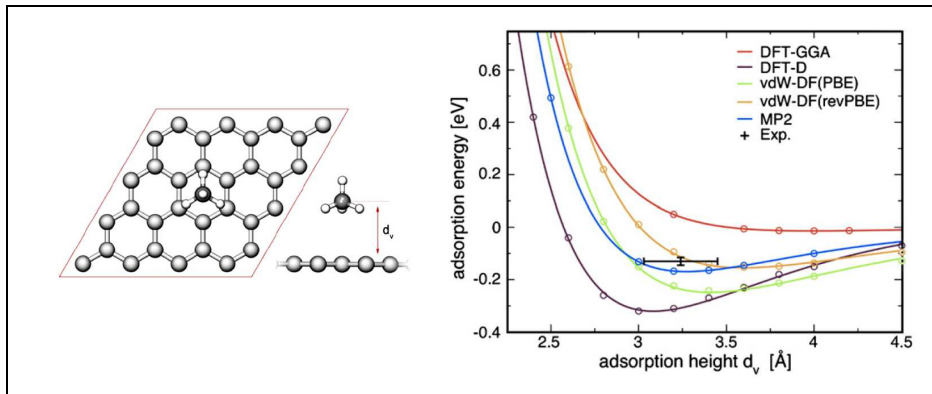
MP2 involves matrix elements of the perturbation between the *HF* reference and all possible excited states. Because the perturbation is a two-electron operator, all matrix elements involving triple, quadruple etc. excitations are zero. Matrix elements with singly excited states are zero due to Brillouins theorem

$$\Rightarrow W_2 = \sum_{i < j}^{occ} \sum_{a < b}^{virtual} \frac{\langle \Phi_0 | \hat{V}_{ee} \Phi_{ii}^{ab} \rangle \langle \Phi_{ij}^{ab} | \hat{V}_{ee} \Phi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

Koopman's theorem + Expression in MOs

$$\begin{aligned} &\downarrow \\ &= \sum_{i < j}^{occ} \sum_{a < b}^{virtual} \left\{ \int \frac{\phi_i(r_1) \phi_j(r_2) \phi_a(r_1) \phi_b(r_2)}{|r_1 - r_2|} d^3 r_1 d^3 r_2 \right. \\ &\quad \left. - \int \frac{\phi_i(r_1) \phi_j(r_2) \phi_b(r_1) \phi_a(r_2)}{|r_1 - r_2|} d^3 r_1 d^3 r_2 \right\}^2 \\ &\quad \times \frac{1}{\varepsilon_i - \varepsilon_j - \varepsilon_a - \varepsilon_b} \end{aligned}$$

MP2 typically accounts for $\sim 80-90\%$ of the correlation energy and is the most economical method for including electron correlation. Notably it also accounts for van der Waals interaction that is difficult to describe within density-functional theory, see figure below, where the adsorption height and adsorption energy of methane at graphene has been calculated (from C. Thierfelder, M. Witte, S. Blankenburg, E. Rauls, W.G. Schmidt, Surf. Sci. **605**, 746 (2011).)

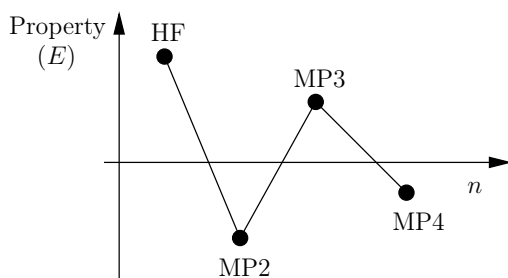


scaling behaviour of *MPn* with number of basis functions *M*

| | | |
|-----|-------|--|
| MP2 | M^5 | } restricted to very small systems, rarely used for practical calculations |
| MP3 | M^6 | |
| MP4 | M^7 | |
| MP5 | M^8 | |
| MP6 | M^9 | |

Remarks

- (i) Møller-Plesset choice of H_0 and H' is not at all consistent with the basic assumption that the perturbation is small: $H' \not\ll H_0$
- (ii) CI methods determine the energy by a variational procedure, and the energy is consequently an upper bound to the exact energy. There is no such guarantee for perturbation methods!
- (iii) Properties calculated within MPn typically oscillate with n :



For "well-behaved" systems the correct answer is normally somewhere between the MP3 and MP4 results.

- (iv) MP methods are size extensive.
- (v) more acronyms:
 MP perturbation theory starting from unrestricted HF \rightarrow **UMPn**
 MP2 starting from CASSCF
 \rightarrow **CASMP2** or **CASPT2**

6.3. Coupled Cluster Methods

Perturbation methods add *all types of correlations* (S, D, T, Q, etc.) to the reference wave function *to a given order* (2, 3, 4, etc.). The idea in *Coupled Cluster* (CC) methods is to include *all correlations of a given type to infinite order*. Let us start by defining an excitation operator **T**

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \dots + \mathbf{T}_{N_{elec}} \quad (144)$$

The \mathbf{T}_i operator acting on an HF reference wave function Φ_0 generates all *ith* excited Slater determinants.

$$\mathbf{T}_1\Phi_0 = \sum_i^{occ} \sum_a^{vir} t_i^a \Phi_i^a \quad (145)$$

$$\mathbf{T}_2\Phi_0 = \sum_{i<j}^{occ} \sum_{a<b}^{vir} t_{ij}^{ab} \Phi_{ij}^{ab} \quad (146)$$

In coupled cluster theory it is customary to use the term *amplitudes* for the expansion coefficients t , which are equivalent to the a_i coefficients in the CI wave function. Using intermediate normalization, a CI wave function can be generated by allowing the excitation operator to work on an HF function.

$$\Psi_{CI} = (1 + \mathbf{T})\Phi_0 = (1 + \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \mathbf{T}_4 + \dots)\Phi_0 \quad (147)$$

The corresponding coupled cluster wave function, on the other hand, is defined as

$$\Psi_{CC} = e^{\mathbf{T}}\Phi_0 \quad (148)$$

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \frac{1}{6}\mathbf{T}^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!}\mathbf{T}^k \quad (149)$$

From eqs. 144 and 149 the exponential operator may be written as

$$\begin{array}{l}
 e^{\mathbf{T}} = \mathbf{1} + T_1 + \underbrace{\left(T_2 + \frac{1}{2}T_1^2\right)}_{\text{generates all doubly excited states, which may either "connected" (T}_2\text{) or "disconnected" (T}_1^2\text{)}} + \left(T_3 + T_2T_1 + \frac{1}{6}T_1^3\right) \\
 \begin{array}{ccc}
 \swarrow & \searrow & \searrow \\
 \text{generates HF} & \text{generates all singly excited states} & \text{generates all doubles, which may either} \\
 & & \text{"connected" (T}_2\text{) or "disconnected" (T}_1^2\text{)} \\
 & & + \left(T_4 + T_3T_1 + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4\right) + \dots
 \end{array}
 \end{array}$$

The first term generates the reference HF and the second all singly excited states. The first parenthesis generates all doubly excited states, which may be considered as *connected* (\mathbf{T}_2) or *disconnected* \mathbf{T}_1^2 . The second parenthesis generates all triply excited states, which again may be either "true" (\mathbf{T}_3) or "product" triples ($\mathbf{T}_2\mathbf{T}_1$), \mathbf{T}_1^3 . The quadruply excited states can similarly be viewed as composed of five terms, a true quadruple and four product terms. Physically, a connected type such as \mathbf{T}_4

corresponds to four electrons interacting simultaneous, while a disconnected term such as \mathbf{T}_2^2 corresponds to two non-interacting pairs of interacting electrons. By comparison with the CI wave function, it is seen that the CC wave function at each excitation level contains additional terms arising from products of excitation. With the coupled cluster wave function in eq. 148 the Schrödinger equation becomes

$$\mathbf{H}e^T\Phi_0 = Ee^T\Phi_0 \quad (150)$$

At this point, one could proceed analogously to CI and evaluate the energy as an expectation value of the CC wave function, and use the variational principle to determine the amplitudes.

$$E_{cc}^{var} = \frac{\langle \Psi_{CC} | \mathbf{H} | \Psi_{CC} \rangle}{\langle \Psi_{CC} | \Psi_{CC} \rangle} = \frac{\langle e^T \Phi_0 | \mathbf{H} | e^T \Phi_0 \rangle}{\langle e^T \Phi_0 | e^T \Phi_0 \rangle} \quad (151)$$

$$E_{cc}^{var} = \frac{\left\langle (1 + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \dots + \frac{1}{N!}\mathbf{T}^N) \Phi_0 | \mathbf{H} | (1 + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \dots + \frac{1}{N!}\mathbf{T}^N) \Phi_0 \right\rangle}{\left\langle (1 + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \dots + \frac{1}{N!}\mathbf{T}^N) \Phi_0 | (1 + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \dots + \frac{1}{N!}\mathbf{T}^N) \Phi_0 \right\rangle} \quad (152)$$

Expansion of the numerator and denominator unfortunately leads to a series of non-vanishing terms all the way up to order N_{elec} , which makes a variational coupled cluster approach unmanageable for all but the smallest systems. The standard formulation of coupled cluster theory instead proceeds by *projecting* the coupled cluster Schrödinger equation 150 onto the reference wave function. Multiplying from the left by Φ_0^* and integrating gives

$$\begin{aligned} \langle \Phi_0 | \mathbf{H} e^T | \Phi_0 \rangle &= E_{cc} \langle \Phi_0 | e^T \Phi_0 \rangle \\ \langle \Phi_0 | \mathbf{H} e^T | \Phi_0 \rangle &= E_{cc} \langle \Phi_0 | (1 + \mathbf{T}_1 + \mathbf{T}_2 + \dots) \Phi_0 \rangle \\ E_{cc} &= \langle \Phi_0 | \mathbf{H} e^T | \Phi_0 \rangle \end{aligned} \quad (153)$$

Expanding out the exponential and using the fact that the Hamiltonian operator contains only one- and two-electron operators we get

$$\begin{aligned} E_{cc} &= \langle \Phi_0 | \mathbf{H} (1 + \mathbf{T}_1 + \mathbf{T}_2 + \frac{1}{2}\mathbf{T}_1^2) | \Phi_0 \rangle \\ E_{cc} &= \langle \Phi_0 | \mathbf{H} | \Phi_0 \rangle + \langle \Phi_0 | \mathbf{H} | \mathbf{T}_1 \Phi_0 \rangle + \\ &\quad \langle \Phi_0 | \mathbf{H} | \mathbf{T}_2 \Phi_0 \rangle + \frac{1}{2} \langle \Phi_0 | \mathbf{H} | \mathbf{T}_1^2 \Phi_0 \rangle \\ E_{cc} &= E_0 + \sum_i^{occ} \sum_a^{vir} t_i^a \langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle + \sum_{i < k}^{occ} \sum_{a < b}^{vir} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Phi_0 | \mathbf{H} | \Phi_{ij}^{ab} \rangle \end{aligned} \quad (154)$$

Note that the infinite expansion of the exponential operator in the eqs. for E_{cc} terminates at the 1 and the \mathbf{T}_2 levels, in contrast to \mathbf{T}_N in the eq. for E_{cc}^{var} . Furthermore, when using HF orbitals for constructing the Slater determinants, the first matrix elements are zero (Brillouin's theorem) and the second matrix elements are just two-electron integrals over MOs, leading to

$$E_{cc} = E_0 + \sum_{i < j}^{occ} \sum_{a < b}^{vir} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) (\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle) \quad (155)$$

The coupled cluster correlation energy is therefore determined completely by the singles and doubles amplitudes and the two-electron MO integrals. Equations for the amplitudes can be obtained by projecting the Schrödinger equation onto the space of singly, doubly, triply, etc. excited determinants. While this can be done analogously to the treatment above, a more elegant formulation is possible by using a *similarity transformation* of the Hamiltonian operator. Consider eq. 150 where we multiply from the left by $e^{-\mathbf{T}}$.

$$e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} \Phi_0 = E_{cc} \Phi_0 \quad (156)$$

Just as $e^{\mathbf{T}}$ is an *excitation* operator working on the function to the *right*, $e^{-\mathbf{T}}$ is a *deexcitation* operator working on the function to the *left*. Multiplying with Φ_0^* from the left and integrating leads directly to the energy equation.

$$E_{cc} = \langle \phi_0 | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \phi_0 \rangle \quad (157)$$

The equation above can be considered as the expectation value of a similarity transformed (non-Hermitian) Hamiltonian. Since $e^{-\mathbf{T}}$ tries to generate deexcitations from the reference Φ_0^* , which is impossible, eq. 157 is identical to eq. 153. Equations for the amplitudes are obtained by multiplying with an excited state.

$$\begin{aligned} \langle \Phi_m^e | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Phi_0 \rangle &= 0 \\ \langle \Phi_{mn}^{ef} | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Phi_0 \rangle &= 0 \\ \langle \Phi_{mnl}^{efg} | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Phi_0 \rangle &= 0 \end{aligned} \quad (158)$$

The deexcitation operator $e^{-\mathbf{T}}$ working on $\langle \Phi_m^e |$ now generates the reference wave function in addition to the singly excited state.

$$\langle \Phi_m^e (1 - \mathbf{T}_1) | \mathbf{H} | (1 + \mathbf{T}_1 + (\mathbf{T}_2 + \frac{1}{2} \mathbf{T}_1^2) + (\mathbf{T}_3 + \mathbf{T}_2 \mathbf{T}_1 + \frac{1}{6} \mathbf{T}_1^3)) \Phi_0 \rangle = 0 \quad (159)$$

Only the indicated terms survive in the expansion when the orthogonality of the Slater determinants and the nature of the Hamiltonian operator (only one- and two-electron terms) are considered. The terms involving singly excited states and the reference wave function are again zero owing to Brillouin's theorem, and the remaining terms form a coupled set of equations with single, double and triple amplitudes as the variables. Similarly, $e^{-\mathbf{T}}$ working on $\langle \Phi_{mn}^{ef} |$ generates both the reference and singly excited states, in addition to the doubly excited states.

$$\left\langle \Phi_{mn}^{ef} \left| e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} \right| \Phi_0 \right\rangle = 0$$

$$\left\langle \Phi_{mn}^{ef} (1 - \mathbf{T}_1) - \mathbf{T}_2 + \frac{1}{2} \mathbf{T}_1^2 \left| \mathbf{H} \left(\begin{array}{l} 1 + \mathbf{T}_1 + (\mathbf{T}_2 + \frac{1}{2} \mathbf{T}_1^2) + (\mathbf{T}_3 + \mathbf{T}_2 \mathbf{T}_1 + \frac{1}{6} \mathbf{T}_1^3) + \\ (\mathbf{T}_4 + \mathbf{T}_3 \mathbf{T}_1 + \frac{1}{2} \mathbf{T}_2^2 + \frac{1}{2} \mathbf{T}_2 \mathbf{T}_1^2 + \frac{1}{24} \mathbf{T}_1^4) \Phi_0 \end{array} \right) \right. \right\rangle = 0 \quad (160)$$

The eq. above now in addition has quadruple amplitudes, and additional terms coupling the lower order amplitudes. More equations connecting amplitudes may be obtained by projection against a triple, quadruple, etc., excited determinant.

So far, everything has been exact. If all cluster operators up to \mathbf{T}_N are included in \mathbf{T} , all possible excited determinants are generated and the coupled cluster wave function is equivalent to full CI. This is, as already stated, impossible for all but the smallest systems. The cluster operator must therefore be truncated at some excitation level. When the \mathbf{T} operator is truncated, some of the terms in the amplitude equations will become zero, and the amplitudes derived from these approximate equations will no longer be exact. The energy calculated from these approximate singles and doubles amplitudes will therefore also be approximate. How severe the approximation is depends on how many terms are included in \mathbf{T} . Including only the \mathbf{T}_1 operator does not give any improvement over HF, as matrix elements between the HF and singly excited states are zero. The lowest level of approximation is therefore $\mathbf{T} = \mathbf{T}_2$, referred to as *Coupled Cluster Doubles* (CCD). Compared with the number of doubles there are relatively few singly excited states. Using $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2$ gives the CCSD model, which is only slightly more demanding than CCD, and yields a more complete model. Both CCD and CCSD involve a computational effort that scales as M_{basis}^6 in the limit of a large basis set. The next higher level has $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3$, giving the CCSDT model. This involves a computational effort that scales as M_{basis}^8 and is more demanding than CISDT. It (and higher order methods such as CCSDTQ) can consequently only be used for small systems, and CCSD is the only generally applicable coupled cluster method. Let us look in a bit more detail at the CCSD method. In this case, we have

$$e^{\mathbf{T}_1 + \mathbf{T}_2} = 1 + \mathbf{T}_1 + (\mathbf{T}_2 + \frac{1}{2} \mathbf{T}_1^2) + (\mathbf{T}_2 \mathbf{T}_1 + \frac{1}{6} \mathbf{T}_1^3) + (\frac{1}{2} \mathbf{T}_2^2 + \frac{1}{2} \mathbf{T}_2 \mathbf{T}_1^2 + \frac{1}{24} \mathbf{T}_1^4) + \dots \quad (161)$$

The CCSD energy is given by the general CC equation 155, and amplitude equations are derived from eqs. 158, 159.

All the matrix elements can be evaluated in terms of MO integrals, and the expressions form coupled non-linear equations for the singles and doubles amplitudes. The equations contain terms up to quartic in the amplitudes, e.g. $(t_i^a)^4$ (since \mathbf{H} contains one- and two-electron operators), and must be solved by iterative techniques. Once the amplitudes are known, the energy and wave function can be calculated. The

important aspect in coupled cluster methods is that excitations of higher order than the truncation of the \mathbf{T} operator enter the amplitude equation. Quadruply excited states, for example, are generated by the \mathbf{T}_2^2 operator in CCSD, and they enter the amplitude equations with a weight of given as a *product* of doubles amplitudes. Quadruply excited states influence the doubles amplitudes, and thereby also the CCSD energy. It is the inclusion of the products of excitations that makes coupled cluster theory size extensive. For the case of a single H_2 molecule, a CISD calculation is equivalent to CCSD, and is also equivalent to a full CI calculation. For two H_2 molecules separated by 100\AA , however, a CISD is not equivalent to a full CI (it is missing the T and Q excitations), but a CCSD calculation is still equivalent to a full CI.

\Rightarrow CCSD is size extensive (in contrast to CISD), where the T_2^2 term is missing.

Comparison of electron correlation methods in terms of **accuracy**?

Typically observed:

$$\text{HF} \ll \text{MP2} \approx \text{MP3} < \text{CCD} < \text{CISD} < \text{CCSD} < \text{MP4} < \text{CCSDT}$$

DFT-GGA often gives results of the same or better quality than MP2, at a computational cost similar to HF (for molecules).

6.4. Beyond Slater Determinants

All electron correlation methods based on expanding the N -electron wave function in terms of Slater determinants build from one-electron functions suffer from very slow convergence, i.e., many SDs are needed for accurate results.

Reason?

Singularity of the electron-electron repulsion

$$\frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \quad \text{for } r_{12} \rightarrow 0$$

In fact, the necessity of going beyond the HF approximation is due to the fact that the (correlated) electrons are farther apart than described by the product of their orbital densities.

$\Rightarrow r_{12}$ dependence should be included in Ansatz for wave function

→ **Hylleraas-type wave function** for two-electron systems

$$\psi(r_1, r_2) = e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} \sum_{klm} c_{klm} (r_1 + r_2)^k (r_1 - r_2)^l r_{12}^m$$

variationally optimize the α_i and c_{klm}

→ extremely accurate results, for example dissociation energy of H_2 converged down to 10^{-9} a.u., i.e., more accurate than can be determined experimentally
 N -electron wave function

→ **R12 methods** by Kutzelnigg & Klopper [*J. Chem. Phys.* **94**, 1985 (1991)]

$$\psi_{R12} = \Phi_{HF} + \sum_{ijab} a_{ijab} \Phi_{ij}^{ab} + \sum_{ij} b_{ij} r_{ij} \Phi_{HF}$$

↑

doubles very
important,
cf. example (1)
in chapter 6.1

↑

electron
distance

R_{12} wave function may be used in connection with the CI, MBPT or CC methods

6.5. Excited Electronic States

By now we have focused on the electronic ground state
 when considering excited states it is useful to distinguish between two cases:

- (i) excited state has same symmetry as ground state
- (ii) excited state has different symmetry

Case (ii) is trivial: The lowest energy state of a given symmetry may be handled completely analogously to the ground state.

Case (i) is non-trivial: It will be difficult to generate a HF type wave function for such a state, because the variational optimization will collapse to the lowest energy solution of the given symmetry

⇒ MBPT & CC methods can not easily applied, because we have no reference wave function

It is, however, relatively easy to generate higher energy states by CI methods

→ simply take the higher eigenvalues from the diagonalization of the CI matrix

⇒ The lowest level of theory for a qualitative description of excited states is obviously CIS. CIS gives wave function of roughly HF quality for excited states (no orbital relaxation!)

→ better results can be obtained from CISD and CASPT2.

In recent years, however, TDDFT seems to be becoming the method of choice for calculating excited states in quantum chemistry (cf. chapter 5).

Example: Energies for lowest singlet excited states of benzene (in eV):

| Exp. | CIS | TDDFT BPW91 | B3LYP |
|------|-----|----------------|-------|
| 4.9 | 6.2 | 5.2 | 5.4 |
| 6.2 | 6.3 | 5.9 | 6.1 |
| 6.3 | 7.1 | 6.3 | 6.3 |
| 6.9 | 7.4 | 6.9 | 6.8 |

[R. E. Stratman, G. E. Sanseria & M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998)]

Comparison with the accuracies typically achieved by electron propagator techniques derived from the Hedin equations (GW and Bethe-Salpeter-type approaches, see, e.g. WG Schmidt, S Glutsch, PH Hahn, F Bechstedt, *Phys. Rev. B* **67**, 085307 (2003); PH Hahn, WG Schmidt, F Bechstedt, *Phys. Rev. B* **72**, 245425 (2005)) shows that the latter are worthwhile trying!

7. Basis Sets

In computational chemistry there are two types of basis functions commonly used:

1. Slater Type Orbitals (STO)

$$\chi_{\xi,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \varphi)r^{n-1}e^{-\xi r}$$

N : normalization constant

Y_{lm} : spherical harmonics

- ▶ exponential dependence $e^{-\xi r}$ as in exact orbitals for H atom
- ▶ no radial nodes, radial nodes introduced by making linear combinations of STOs
- ▶ primarily used for atomic and diatomic systems where high accuracy is required

2. Gaussian Type Orbitals (GTO)

in polar coordinates

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \varphi)r^{2n-2-l}e^{-\zeta r^2}$$

in cartesian coordinates

$$\chi_{\zeta,l_x,l_y,l_z}(x, y, z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2}$$

$e^{-\zeta r^2}$ term \rightarrow 2 problems:

- ▶ zero slope at the nucleus
- ▶ falls off too rapidly far from the nucleus

\Rightarrow need more GTOs to obtain same accuracy as with STOs (roughly three times more)

Still, in quantum chemistry GTOs are predominantly used!

Why?

HF leads to one-electron integrals

$$\int \chi_{\alpha}(1) \left(-\frac{\nabla^2}{2} \right) \chi_{\beta}(1) d^3r_1$$

$$\int \chi_{\alpha}(1) \frac{Z_a}{|R_A - r_1|} \chi_{\beta}(1) d^3r_1$$

and two-electron integrals

$$\int \chi_{\alpha}(1) \chi_{\beta}(2) \frac{1}{|r_1 - r_2|} \chi_{\gamma}(1) \chi_{\delta}(2) d^3r_1 d^3r_2$$

for M basis functions we have

$$\begin{aligned} O(M^2) & \text{ one-electron integrals and} \\ O(M^4) & \text{ two-electron integrals} \end{aligned}$$

The two electron integrals may have 1,2,3 or 4 different atomic centers.

The calculation of especially 3- and 4-centre two-electron integrals is very time-consuming for exponential functions

GTOs are better suited for calculating two-electron integrals, because the product of two Gaussian located two different positions R_A and R_B with different exponents α and β can be written a a single Gaussian located between R_A and R_B :

$$\begin{aligned} \chi_A(r) &= \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha(r-R_A)^2} \\ \chi_B(r) &= \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}} e^{-\beta(r-R_B)^2} \end{aligned}$$

$$\Rightarrow \chi_A(r)\chi_B(r) = Ke^{-\gamma(r-R_C)^2}$$

$$\text{with } \gamma = \alpha + \beta$$

$$R_C = \frac{\alpha R_A + \beta R_B}{\alpha + \beta}$$

$$K = \left(\frac{2}{\pi}\right)^{\frac{3}{2}} (\alpha\beta)^{\frac{3}{4}} e^{-\frac{\alpha\beta}{\alpha+\beta}(R_A+R_B)^2}$$

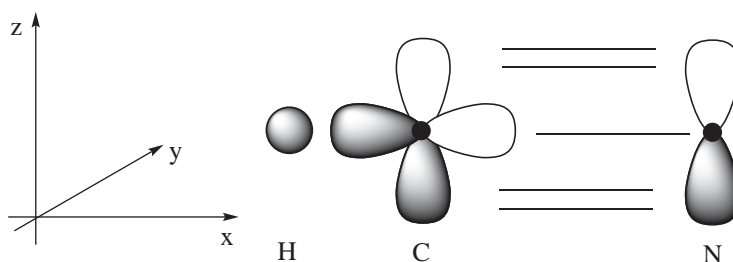
\Rightarrow allows compact formulas for all types of one- and two-electron integrals

\Rightarrow The increase in number of basis functions compared to STOs is more than compensated for by the reduction of CPU time required for evaluating the integrals

\Rightarrow GTOs are used almost universally in quantum chemistry calculations

How many basis functions?

- ▶ smallest number possible \rightarrow **minimum basis set**
 (only enough functions to contain all electrons of the neutral atoms)
 $H, He \rightarrow$ one s -function
 first-row elements $\rightarrow 1s, 2s, 2p_x, 2p_y, 2p_z$
- ▶ doubling of all basis functions \rightarrow **Double Zeta (DZ) basis**
 (name comes from exp.: $e^{-\zeta r}$)
 $H, He \rightarrow 1s, 1s'$
 first row $\rightarrow 1s, 1s', 2s, 2s', 2p, 2p'$


Example: HCN

$C - H$ σ -bond formed between C and H relatively short
 $C - N$ π -bonded with relatively diffuse p -orbitals

\Rightarrow tight p_x -orbitals for C
 extended p_y, p_z -orbitals for C

\Rightarrow much better described with two different exponentials

- ▶ chemical bonding occurs between valence orbitals
 core orbital barely affected by bonding
 \rightarrow only double the number of valence orbitals
 \rightarrow **split valence basis, valence double zeta (VDZ)**
- ▶ next step up in basis set size \rightarrow **Triple Zeta (TZ)**
triple split valence basis set
 accordingly -Quadruple Zeta (QZ)
 -Quintuple Zeta (5Z)
- ▶ Electron correlation describes the energy lowering by the electrons "avoiding" each other, beyond the average effect taken into account by HF methods. Chemists identify two types of correlation, an "in-out" and an "angular" correlation. The "in-out" or "radial" correlation refers to the situation where one electron is close to, and the other far from the nucleus.
 \rightarrow This is accounted for by different exponents
 "Angular" correlation refers to the situation where two electrons are on opposite sides of the nucleus
 \rightarrow to describe this the basis set needs functions of different angular momenta

Example: HCN Hydrogen s -orbitals are not spherically symmetric, they are "polarized"
 \rightarrow describe this by p -orbitals localized at H

⇒ **polarization functions** (functions with higher angular momentum)

→ **Double Zeta plus Polarization (DZP)**
Double Zeta plus Double Polarization (DZ2P)

- ▶ **mixed basis sets** high number of basis functions on the "interesting" part of the molecule and minimum basis for the rest

Problem: variational principle will place the electrons near the centre with the most basis functions

→ H_2 molecule with a minimum basis at one end and a DZ basis at the other will have a dipole!

- ▶ **Contracted Basis Sets**

Optimization of all variational parameters in all GTO is very time consuming. Core electrons are anyway little dependent on chemical environment.

→ make variational coefficients in front of the inner basis functions constant

→ reduce the degrees of freedom by forming linear combinations of **primitive GTOs (PGTOs)** into a smaller set of functions known as **contracted GTOs (CGTOs)**

$$\chi^{CGTO} = \sum_i a_i \chi_i^{PGTO}$$

The degree of contraction is the number of PGTOs entering the CGTO, typically between 1 and 10. The specification of a basis set in terms of primitive and contracted functions is given by the notation

$$\left(\underbrace{10s \ 4p \ 1d}_{\substack{\text{primitive} \\ \text{first-row} \\ \text{elements}}} \ / \ \underbrace{4s \ 1p}_{\text{hydrogen}} \right) \rightarrow \left[\underbrace{3s \ 2p \ 1d}_{\substack{\text{contracted} \\ \text{functions} \\ \text{for first-row} \\ \text{elements}}} \ / \ \underbrace{2s \ 1p}_{\text{hydrogen}} \right]$$

- ▶ **Pople Style Basis Sets**

STO-nG: minimum type basis where the exponents of the PGTO are determined by fitting to the STO, rather than by optimizing them variationally, each STO is represented by n PGTOs

[Hehre, Steward, Pople, *J. Chem. Phys.* **51**, 2657 (1969)]

3-21 G: split valence basis:

3 PGTOs → core orbitals
 2 PGTOs → inner part valence
 1 PGTO → outer part valence

[Binkeley & Pople, *J. Am. Chem. Soc.* **102**, 939 (1980)]

6-31 G: 6 PGTOs → core
 3 PGTOs → inner valence
 1 PGTO → outer valence

(same number of contracted basis functions as 3-21 G, but more primitive GTOs)

6-311 G: split valence into three functions, respresented by 3,1, and 1 PGTO

To each of basis sets we can add diffuse and/or polarization functions

+ → one set of diffuse *s*- and *p*-function on heavy atoms

++ → diffuse functions also on hydrogen

Polarization functions are indicated after the G

Examples:

−6 − 31 + $G(d)$ diffuse *sp*-functions and *d*-types polarization functions on heavy atoms only

−6 − 311 + + $G(3df, 3pd)$ largest standard Pople style basis set with diffuse functions both on heavy and hydrogen atoms and 3*d*- and one *f*- polarization functions on heavy atoms and 3*d*- and one *d*-polarization function on hydrogen

One major reason for the popularity of the Pople style basis sets is the extensive calibration available.

→ self-sustaining procedure

► Atomic Natural Orbitals (ANO) Basis Sets

calculation of the free atom (typically at CISD level) with a large number of PGTO

contraction to a small number of CGTOs on the basis of the occupation numbers

[*J. Almöt & P. R. Taylor, J. Chem. Phys.* **92**, 551 (1990);

Adv. Quantum Chem. **22**, 301 (1991)]

► Correlation Consistent Basis Sets (cc)

[*T. H. Dunning, J. Chem. Phys.* **90**, 1007 (1989),

R. A. Kendall, T. H. Dunning and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992)]

cc-basis sets are designed so that functions which contribute similar amounts of

correlation energy are included at the same stage, independent of the function type.

Example:

$$E_c(1d) < E_c(2d) \approx E_c(1f) < E_c(3d) \approx E(2f) \\ \approx E(1g)$$

→ addition of polarization functions in the order

$$1d, 2d1f, 3d2f1g$$

Augmentation by additional diffuse functions

→ aug-cc Basis sets

(augmentation consists of adding one extra function with a smaller exponent for each angular momentum)

Augmentation by additional tight functions also done for better description of core correlation

Examples:

| Basis | Primitive functions | Contracted functions |
|---------|--|---|
| cc-pVDZ | 9s, 4p, 1d/4s, 1p | 3s, 2p, 1d/2s, 1p |
| cc-pVTZ | 10s, 5p, 2d, 1f/5s, 2p, 1d | 4s, 3p, 2d, 1f/3s, 2p, 1d |
| cc-pVQZ | 16s, 10p, 5d, 4f, 3g, 2h, 1i/ 10s, 5p, 4d, 3f, 2g, 1h | 7s, 6p, 5d, 4f, 3g, 2h, 1i/ 6s, 5p, 4d, 3f, 2g, 1h |

The main advantage of the ANO and cc basis sets is the ability to generate a sequence of basis sets which converges towards the basis set limit.

This is not the case for Pople-style basis sets!

Typical recovering of correlation energy:

| | |
|---------|-------|
| cc-pVDZ | ~ 65% |
| cc-pVTZ | ~ 85% |
| cc-pVQZ | ~ 93% |
| cc-pV5Z | ~ 96% |
| cc-pV6Z | ~ 98% |

Further increase makes no sense, because relativistic effects and errors from BOA become more important.

Basis Set Superposition Errors (BSSE)

basis functions typically centered on the nuclei

- ▶ when the nuclei approach other the electron density around one nucleus may be described by functions centered at another nucleus
- ▶ "quality" of basis sets improve for smaller distance
- ▶ correlation energy is artificially lowered
- ▶ bond strength is overestimated
Problem can be avoided theoretically by using a complete basis, obviously not possible in many instances
- ▶ estimate BSSE from calculations where the basis functions of the other atoms are present, but **not** the respective nuclei ("ghost orbitals"). This is known as **Counterpoise (CP)** correlation.
[F. B. van Duijneveldt et al. Chem. Rev. 94, 1873 (94)]

8. Beyond non-relativistic calculations

8.1. Electron spin

energy of an electron in a hydrogen-like system (one nucleus & one electron)

$$E = -\frac{Z^2}{2} \stackrel{!}{=} -\frac{1}{2}mv^2$$

$$\Rightarrow v = Z \text{ (in a.u.)}$$

$$c = 137 \text{ (in a.u.)}$$

\Rightarrow core electrons in heavy nuclei experience relativistic effects

$$m = m_0 \left(\sqrt{1 - \frac{v^2}{c^2}} \right)^{-1}$$

get heavier

\rightarrow 1s orbitals shrinks in size

\rightarrow more effective screening of the core

\rightarrow higher angular momentum orbitals expand in size

\Rightarrow elements from the fifth (actually also from the fourth) row of the periodic table should be calculated using relativistic corrections

Dirac proposed to replace the SE for free electrons by

$$\{c\vec{\alpha} \cdot \vec{p} + \hat{\beta}mc^2\}\psi = i\frac{\partial\psi}{\partial t}$$

where

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\sigma_i = \begin{cases} \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{cases} \quad \vec{p} = -i\vec{\nabla}$$

The σ_i matrices can be viewed as representations of the $\hat{S}_x, \hat{S}_y, \hat{S}_z$ spin operators

$$\left. \begin{array}{l} \alpha \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \beta \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{array} \right\} \text{spin functions, } \hat{S}_i = \frac{1}{2}\sigma_i$$

$$\Rightarrow \hat{S}_z\alpha = \frac{1}{2}\alpha, \quad \hat{S}_z\beta = -\frac{1}{2}\beta$$

$$\Rightarrow \alpha, \beta \text{ are eigenfunctions of the } s_z \text{ operator with eigenvalues } \pm\frac{1}{2}$$

Short excursion to spin algebra

$$\hat{S}_x\alpha = \frac{1}{2}\beta$$

$$\hat{S}_x\beta = \frac{1}{2}\alpha$$

$$\hat{S}_y\alpha = \frac{i}{2}\beta$$

$$\hat{S}_y\beta = -\frac{i}{2}\alpha$$

$$\hat{S} = \hat{S}_x + \hat{S}_y + \hat{S}_z \Rightarrow \begin{aligned} \hat{S}^2\alpha &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha \\ \hat{S}^2\beta &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) \beta \end{aligned}$$

$$\Rightarrow \alpha, \beta \text{ are also eigenfunctions of the operator } S^2 \text{ with eigenvalues } S(S+1)$$

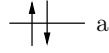
For an N -electron spin function, the total spin angular momentum is additive

$$\hat{S} = \sum_{i=1}^N \hat{S}(i),$$

the individual Cartesian components of the spin angular momentum are also additive

$$\hat{S}_z\psi = \sum_{i=1}^N S_z(i)\psi$$

$$\begin{aligned} \hat{S}^2 &= \sum_{i=1}^N \hat{S}^2(i) + 2 \sum_{i<j}^N (\hat{S}_x(i)\hat{S}_x(j) + \hat{S}_y(i)\hat{S}_y(j) \\ &\quad + \hat{S}_z(i)\hat{S}_z(j)) \end{aligned}$$

Examples:(i) both electrons are spin-paired in the same orbital a 

$$\begin{aligned}\psi &= \frac{1}{\sqrt{2}} \begin{bmatrix} a(1)\alpha(1) & a(1)\beta(1) \\ a(2)\alpha(2) & a(2)\beta(2) \end{bmatrix} \\ &= \frac{1}{\sqrt{2}} a(1)a(2) \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}\end{aligned}$$

$$\begin{aligned}\langle \psi | \hat{S}^2 | \psi \rangle &= \frac{1}{2} \langle \overbrace{a^2(1)a^2(2)}^1 \rangle \\ &\times \langle \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \} | \hat{S}^2 | \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \} \rangle \\ &= \frac{1}{2} \left[\langle \alpha(1)\beta(2) | \hat{S}^2 | \alpha(1)\beta(2) \rangle - \right. \\ &\quad \langle \alpha(1)\beta(2) | \hat{S}^2 | \alpha(2)\beta(1) \rangle - \\ &\quad \langle \alpha(2)\beta(1) | \hat{S}^2 | \alpha(1)\beta(2) \rangle + \\ &\quad \left. \langle \alpha(2)\beta(1) | \hat{S}^2 | \alpha(2)\beta(1) \rangle \right]\end{aligned}$$

$$\begin{aligned}\hat{S}^2 \alpha(1)\beta(2) &= \hat{S}^2(1)\alpha(1)\beta(2) + \hat{S}^2(2)\alpha(1)\beta(2) \\ &\quad + 2\hat{S}_x(1)\hat{S}_x(2)\alpha(1)\beta(2) \\ &\quad + 2\hat{S}_y(1)\hat{S}_y(2)\alpha(1)\beta(2) \\ &\quad + 2\hat{S}_z(1)\hat{S}_z(2)\alpha(1)\beta(2) \\ &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) \\ &\quad + \frac{1}{2} \beta(1)\alpha(2) + \frac{1}{2} \beta(1)\alpha(2) - \frac{1}{2} \alpha(1)\beta(2)\end{aligned}$$

Similarly

$$\begin{aligned}\hat{S}^2 \alpha(2)\beta(1) &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(2)\beta(1) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(2)\beta(1) \\ &\quad + \frac{1}{2} \beta(2)\alpha(1) + \frac{1}{2} \beta(2)\alpha(1) - \frac{1}{2} \alpha(2)\beta(1)\end{aligned}$$

evaluate now

$$\begin{aligned}
 & \langle \alpha(1)\beta(2) | \hat{S}^2 | \alpha(1)\beta(2) \rangle \\
 &= \int \int d1d2 \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) \\
 &+ \int \int d1d2 \alpha(1)\beta(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\beta(2) \\
 &+ \int \int d1d2 \alpha(1)\beta(2) \frac{1}{2} \beta(1)\alpha(2) \\
 &+ \int \int d1d2 \alpha(1)\beta(2) \frac{1}{2} \beta(1)\alpha(2) \\
 &- \int \int \alpha(1)\beta(2) \frac{1}{2} \alpha(1)\beta(2) \\
 &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) + 0 + 0 - \frac{1}{2} \\
 &= 1
 \end{aligned}$$

Similarly

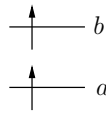
$$\begin{aligned}
 \langle \alpha(1)\beta(2) | \hat{S}^2 | \alpha(2)\beta(1) \rangle &= 1 \\
 \langle \alpha(2)\beta(1) | \hat{S}^2 | \alpha(2)\beta(1) \rangle &= 1 \\
 \langle \alpha(2)\beta(1) | \hat{S}^2 | \alpha(1)\beta(2) \rangle &= 1
 \end{aligned}$$

⇒ collect all terms

$$\boxed{\langle \psi | S^2 | \psi \rangle = 0} \quad \text{no big surprise!}$$

→ **singlet wave function**

(ii) two α -spin electrons in two different spatial orbitals

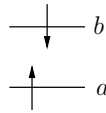


$$\begin{aligned}
 \psi &= \frac{1}{\sqrt{2}} \begin{bmatrix} a(1)\alpha(1) & b(1)\alpha(1) \\ a(2)\alpha(2) & b(2)\alpha(2) \end{bmatrix} \\
 &= \frac{1}{\sqrt{2}} \alpha(1)\alpha(2) \{ a(1)b(2) - a(2)b(1) \}
 \end{aligned}$$

$$\begin{aligned}
 2 \cdot \langle \psi | S^2 \psi \rangle &= \langle \alpha(1)\alpha(2) | S^2 \alpha(1)\alpha(2) \rangle \\
 &= \int \int d1 d2 \alpha(1)\alpha(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\alpha(2) \\
 &\quad + \int \int d1 d2 \alpha(1)\alpha(2) \frac{1}{2} \left(\frac{1}{2} + 1 \right) \alpha(1)\alpha(2) \\
 &\quad + \int \int d1 d2 \alpha(1)\alpha(2) \frac{1}{2} \beta(1)\beta(2) \\
 &\quad - \int \int d1 d2 \alpha(1)\alpha(2) \frac{1}{2} \beta(1)\beta(2) \\
 &\quad + \int \int \alpha(1)\alpha(2) \frac{1}{2} \alpha(1)\alpha(2) \\
 &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) + 0 - 0 + 1 \\
 &= 4
 \end{aligned}$$

$$\Rightarrow \langle \psi | S^2 \psi \rangle = 2 \quad \rightarrow \text{triplet wave function}$$

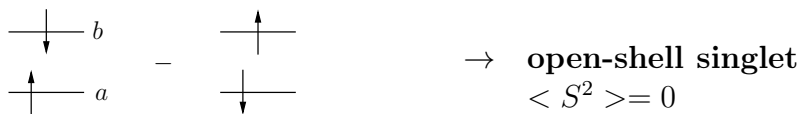
(iii)



$$\begin{aligned}
 \psi &= \frac{1}{\sqrt{2}} \begin{bmatrix} a(1)\alpha(1) & b(1)\beta(1) \\ a(2)\alpha(2) & b(2)\beta(2) \end{bmatrix} \\
 &= \frac{1}{\sqrt{2}} \{ a(1)\alpha(1)b(2)\beta(2) - a(2)\alpha(2)b(1)\beta(1) \}
 \end{aligned}$$

$$\langle \psi | S^2 \psi \rangle = 1, \quad \psi \text{ is not an eigenfunction of } S^2$$

\Rightarrow form linear combinations, state must be described by a superposition of two Slater determinants

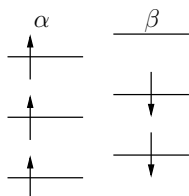


$$\psi = \frac{1}{2}[a(1)b(2) + a(2)b(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$



(iv) UHF wave function

spatial orbitals are not necessarily orthogonal to one another, only within each spin set



$$\Rightarrow \langle \psi^{UHF} | S^2 | \psi^{UHF} \rangle$$

$$= \frac{n_\alpha - n_\beta}{2} \left(\frac{n_\alpha - n_\beta}{2} + 1 \right) + n_\beta - \sum_{\substack{i \in \alpha \\ j \in \beta}}^{occ} \langle \phi_i | \phi_j \rangle^2$$

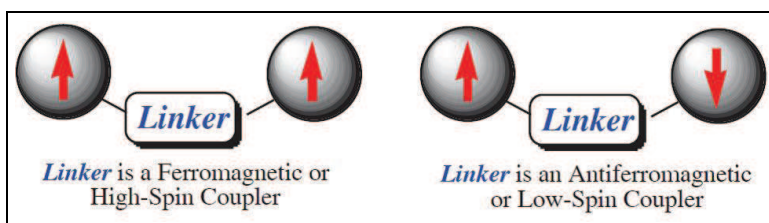
→ mixture of spin-states possible

→ "spin-contaminated" wave functions

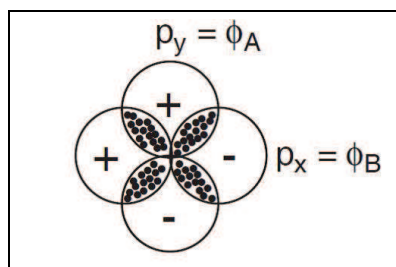
Already from the symmetry properties of the spin orbitals we can learn much about the molecular spin structure.

Example: Singlet and triplet energies for biradicals:

A biradical can be thought of as two spin-containing units bridged by an exchange-coupling unit:



The π -topology and conformation of the biradical are central to understanding the electronic structure, i.e., whether the ground-state is a triplet (above left) or a singlet (above right). Consider two electrons in two orbitals, ϕ_A and ϕ_B (e.g., two orthogonal 2p orbitals).



A first trial wavefunction for this system is

$$\psi = \phi_A(1)\phi_B(2). \quad (162)$$

Because it violates the Pauli exclusion principle, ψ is an unacceptable wavefunction. Rather we have to consider the linear combinations of ψ and ψ' where $\psi' = \phi_A(2)\phi_B(1)$

$$\begin{aligned} \psi_+ &= 0.707 [\psi + \psi'] && (0.707 \text{ is the normalization factor}) \quad (163) \\ &= 0.707 [\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)] \end{aligned}$$

and

$$\begin{aligned}\psi_- &= 0.707 [\psi - \psi'] \quad (0.707 \text{ is the normalization factor}) \quad (164) \\ &= 0.707 [\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]\end{aligned}$$

Obviously permutation of the electrons yields

$$P_{12}\psi_- = 0.707 [\psi_A(2)\psi_B(1) - \psi_B(2)\psi_A(1)] = -\psi_- \quad (165)$$

Upon inspection, it is clear that the permuted ψ_- is $-\psi_-$. Therefore, ψ_- is an acceptable wavefunction. Thus, there are two acceptable wavefunctions for two electrons in two different orbitals.

$$\psi_+ = 0.707 [\psi + \psi'] \quad (166)$$

$$\psi_- = 0.707 [\psi - \psi'] \quad (167)$$

Because permuted ψ_+ is equal to ψ_+ , ψ_+ is called a symmetric spatial wavefunction (spatial because the wavefunction describes the motion of the electron in a particular region of space). By the same token, because permuted ψ_- is equal to $-\psi_-$, ψ_- is called an antisymmetric spatial wavefunction.

Now, let's consider that the total wave function is a product of spatial (ψ) and spin wavefunctions (γ). The total wavefunction must be antisymmetric with respect to electron exchange.

$$\Psi_{tot} = \psi_{space}\gamma_{spin} \quad (168)$$

$$P_{12}\Psi_{tot} = \Psi_{tot} \quad (169)$$

Spin wavefunctions describe the spin angular momentum of the electrons. For two spins, the conceivable wavefunctions are:

$$\gamma \uparrow\uparrow,+ = \alpha(1)\alpha(2) \quad (170)$$

$$\gamma \downarrow\downarrow,+ = \beta(1)\beta(2) \quad (171)$$

$$\gamma \uparrow\downarrow,+ = 0.707 [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (172)$$

and

$$\gamma \uparrow\downarrow,- = 0.707 [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (173)$$

The origin of equations 172 and 173 are similar to their spatial counterparts, and the rules for creating the spin wavefunctions are the same as those for creating allowable spatial wavefunctions. Again, by inspection, spin wavefunctions 170 - 172 are symmetric and spin wavefunction 173 is antisymmetric.

Because the Ψ_{tot} must be antisymmetric, the allowed total wavefunctions are:

$$\Psi_{tot} = \psi_{-\gamma} \uparrow\uparrow_{,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (174)$$

$$\Psi_{tot} = \psi_{-\gamma} \downarrow\downarrow_{,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (175)$$

$$\Psi_{tot} = \psi_{-\gamma} \uparrow\downarrow_{,+} \quad (\text{antisymmetric spatial and symmetric spin}) \quad (176)$$

$$\Psi_{tot} = \psi_{+\gamma} \uparrow\downarrow_{,-} \quad (\text{symmetric spatial and antisymmetric spin}) \quad (177)$$

The first three total wavefunctions 174 - 176 correspond to the three microstates of the **triplet** manifold, while the final total wavefunction 177 corresponds to an open-shell **singlet** state. Most notable is that the *triplet* states have antisymmetric spatial wavefunctions while the *singlet* state has a symmetric *spatial* wavefunction. The reason that this is noteworthy is that it is the spatial wavefunctions that are used to determine energies. In fact, the energies we wish to compute are the electron-electron repulsion energies since these are the essence of the energy difference between the *singlet* and *triplet* states.

Two closed-shell zwitterionic singlet states are also possible ($\psi_{S+,CS}$ and $\psi_{S-,CS}$), and are given below. In what follows, the ϕ has been dropped from the designations for the orbitals. Therefore, from two orbitals and two electrons, a total of four electronic states are formed (thereby we do not differentiate between the three spin triplets, otherwise we had six states)

$$\psi_A = \frac{1}{\sqrt{2}}(a(1)b(2) - b(1)a(2)) \quad \text{Triplet} \quad (178)$$

$$\psi_{S,OS} = \frac{1}{\sqrt{2}}(a(1)b(2) + b(1)a(2)) \quad \text{Open-shell Singlet} \quad (179)$$

$$\psi_{S+,CS} = \frac{1}{\sqrt{2}}(a(1)a(2) + b(1)b(2)) \quad \text{Closed-shell Singlet} \quad (180)$$

$$\psi_{S-,CS} = \frac{1}{\sqrt{2}}(a(1)a(2) - b(1)b(2)) \quad \text{Closed-shell Singlet} \quad (181)$$

Next, let's use an approximate zero-order Hamiltonian, given by the sum of one-electron energy operators, and calculate the energies of the four states.

$$H^0 = h(1) + h(2) \quad (182)$$

The energy of the triplet is:

$$\begin{aligned}
E^0(\psi_A) &= \frac{1}{2} \langle a(1)b(2) - b(1)a(2) | h(1) + h(2) | a(1)b(2) - b(1)a(2) \rangle \\
&= \frac{1}{2} [\langle a(1)b(2) | h(1) + h(2) | a(1)b(2) \rangle - \langle a(1)b(2) | h(1) + h(2) | b(1)a(2) \rangle - \\
&\quad \langle b(1)a(2) | h(1) + h(2) | a(1)b(2) \rangle + \langle b(1)a(2) | h(1) + h(2) | b(1)a(2) \rangle] \\
&= \frac{1}{2} [\langle b(2) | b(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | h(2) | b(2) \rangle \\
&\quad - \langle b(2) | a(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(1) | b(1) \rangle \langle b(2) | h(2) | a(2) \rangle \\
&\quad - \langle a(2) | b(2) \rangle \langle b(1) | h(1) | a(1) \rangle - \langle b(1) | a(1) \rangle \langle a(2) | h(2) | b(2) \rangle \\
&\quad + \langle a(2) | a(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle b(1) | b(1) \rangle \langle a(2) | h(2) | a(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha - 0 - 0 - 0 - 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{183}$$

The energy of the open-shell singlet is:

$$\begin{aligned}
E^0(\psi_{S,OS}) &= \frac{1}{2} \langle a(1)b(2) + b(1)a(2) | h(1) + h(2) | a(1)b(2) + b(1)a(2) \rangle \\
&= \frac{1}{2} [\langle a(1)b(2) | h(1) + h(2) | a(1)b(2) \rangle + \langle a(1)b(2) | h(1) + h(2) | b(1)a(2) \rangle + \\
&\quad \langle b(1)a(2) | h(1) + h(2) | a(1)b(2) \rangle + \langle b(1)a(2) | h(1) + h(2) | b(1)a(2) \rangle] \\
&= \frac{1}{2} [\langle b(2) | b(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle a(1) | a(1) \rangle \langle b(2) | h(2) | b(2) \rangle \\
&\quad + \langle b(2) | a(2) \rangle \langle a(1) | h(1) | b(1) \rangle + \langle a(1) | b(1) \rangle \langle b(2) | h(2) | a(2) \rangle \\
&\quad + \langle a(2) | b(2) \rangle \langle b(1) | h(1) | a(1) \rangle + \langle b(1) | a(1) \rangle \langle a(2) | h(2) | b(2) \rangle \\
&\quad + \langle a(2) | a(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle b(1) | b(1) \rangle \langle a(2) | h(2) | a(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha + 0 + 0 + 0 + 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{184}$$

The energy of the first closed-shell singlet is:

$$\begin{aligned}
E^0(\psi_{S+,CS}) &= \frac{1}{2} \langle a(1)a(2) + b(1)b(2) | h(1) + h(2) | a(1)a(2) + b(1)b(2) \rangle \\
&= \frac{1}{2} [\langle a(1)a(2) | h(1) + h(2) | a(1)a(2) \rangle + \langle a(1)a(2) | h(1) + h(2) | b(1)b(2) \rangle + \\
&\quad \langle b(1)b(2) | h(1) + h(2) | a(1)a(2) \rangle + \langle b(1)b(2) | h(1) + h(2) | b(1)b(2) \rangle] \\
&= \frac{1}{2} [\langle a(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle a(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle \\
&\quad + \langle a(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle + \langle a(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle \\
&\quad + \langle b(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle + \langle b(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle \\
&\quad + \langle b(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle b(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle] \\
&= \frac{1}{2} [\alpha + \alpha + 0 + 0 + 0 + 0 + \alpha + \alpha] = 2\alpha
\end{aligned} \tag{185}$$

The energy of the second closed-shell singlet is:

$$\begin{aligned}
 E^0(\psi_{S-,CS}) &= \frac{1}{2} \langle a(1)a(2) - b(1)b(2) | h(1) + h(2) | a(1)a(2) - b(1)b(2) \rangle \\
 &= \frac{1}{2} [\langle a(1)a(2) | h(1) + h(2) | a(1)a(2) \rangle - \langle a(1)a(2) | h(1) + h(2) | b(1)b(2) \rangle - \\
 &\quad \langle b(1)b(2) | h(1) + h(2) | a(1)a(2) \rangle + \langle b(1)b(2) | h(1) + h(2) | b(1)b(2) \rangle] \\
 &= \frac{1}{2} [\langle a(2) | a(2) \rangle \langle a(1) | h(1) | a(1) \rangle + \langle a(1) | a(1) \rangle \langle a(2) | h(2) | a(2) \rangle \\
 &\quad - \langle a(2) | b(2) \rangle \langle a(1) | h(1) | b(1) \rangle - \langle a(1) | b(1) \rangle \langle a(2) | h(2) | b(2) \rangle \\
 &\quad - \langle b(2) | a(2) \rangle \langle b(1) | h(1) | a(1) \rangle - \langle b(1) | a(1) \rangle \langle b(2) | h(2) | a(2) \rangle \\
 &\quad + \langle b(2) | b(2) \rangle \langle b(1) | h(1) | b(1) \rangle + \langle b(1) | b(1) \rangle \langle b(2) | h(2) | b(2) \rangle] \\
 &= \frac{1}{2} [\alpha + \alpha - 0 - 0 - 0 - 0 + \alpha + \alpha] = 2\alpha
 \end{aligned} \tag{186}$$

So, to zeroth order, all four states have the same energy: 2α . This is obvious by inspection, two electrons in identical orbitals have the same orbital energies (in the absence of electron-electron repulsion) irrespective of how they are occupied. Now, let's use a more realistic perturbed Hamiltonian that accounts for electron-electron repulsion:

$$H = H^{(0)} + H^{(1)} = H^{(0)} + 1/r_{12} \tag{187}$$

and calculate the first-order corrected energies.

The first-order corrected energy of the open-shell triplet is:

$$\begin{aligned}
 E^{(1)}(\psi_A) &= \frac{1}{2} \left\langle a(1)b(2) - b(1)a(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)b(2) - b(1)a(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) - b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) - b(1)a(2) \right\rangle \right. \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle - \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle - \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} [j - k - k + j] = 2\alpha + j - k
 \end{aligned} \tag{188}$$

The first-order corrected energy of the open-shell singlet is:

$$\begin{aligned}
 E^{(1)}(\psi_{S,OS}) &= \frac{1}{2} \left\langle a(1)b(2) + b(1)a(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)b(2) + b(1)a(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) + b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) + b(1)a(2) \right\rangle \right. \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle a(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)a(2) \right\rangle + \right. \\
 &\quad \left. \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)b(2) \right\rangle + \left\langle b(1)a(2) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle + \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \right. \\
 &\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2}[j + k + k + j] = 2\alpha + j + k
 \end{aligned} \tag{189}$$

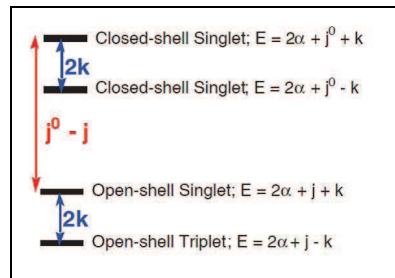
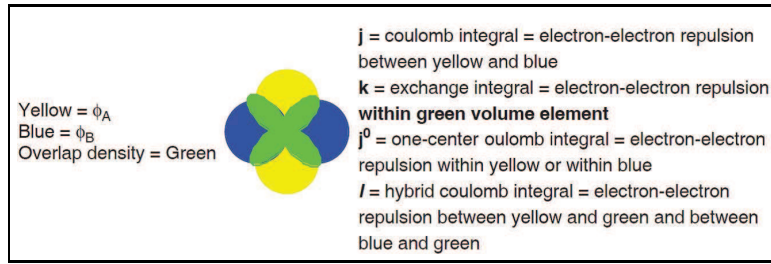
The first-order corrected energy of the first closed-shell singlet is:

$$\begin{aligned}
 E^{(1)}(\psi_{S+,CS}) &= \frac{1}{2} \left\langle a(1)a(2) + b(1)b(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) + b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) + b(1)b(2) \right\rangle \right. \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle + \right. \\
 &\quad \left. \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \\
 &= 2\alpha + \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle + \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle \\
 &\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2}[j^0 + k + k + j^0] = 2\alpha + j^0 + k
 \end{aligned} \tag{190}$$

The first-order corrected energy of the second closed-shell singlet is:

$$\begin{aligned}
 E^{(1)}(\psi_{S-,CS}) &= \frac{1}{2} \left\langle a(1)a(2) - b(1)b(2) \left| H^{(0)} + \frac{1}{r_{12}} \right| a(1)a(2) - b(1)b(2) \right\rangle \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) - b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) - b(1)b(2) \right\rangle \right. \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle - \left\langle a(1)a(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| a(1)a(2) \right\rangle + \left\langle b(1)b(2) \left| \frac{1}{r_{12}} \right| b(1)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2} \left[\left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)a(2) \right\rangle - \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle - \right. \\
 &\quad \left. \left\langle b(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle + \left\langle b(1)b(1) \left| \frac{1}{r_{12}} \right| b(2)b(2) \right\rangle \right] \\
 &= 2\alpha + \frac{1}{2}[j^0 - k - k + j^0] = 2\alpha + j^0 - k
 \end{aligned} \tag{191}$$

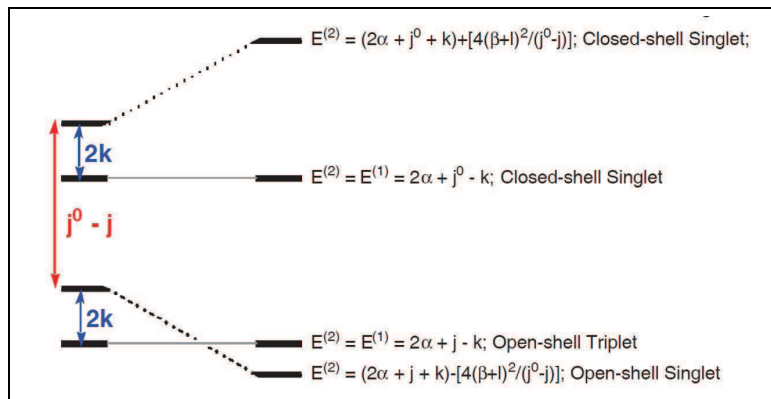
In the last four energy expressions, j is a two-center coulomb integral, k is the exchange integral, and j^0 is the one-center coulomb integral ($j^0 \gg j$). These integrals are displayed pictorially in the figure below.



These energies give the energy level diagram shown above. A better approximation to energy can be obtained by including the second order corrections from perturbation theory:

$$E^{(2)} = \frac{\langle \psi_i | H^{(1)} | \psi_j \rangle^2}{E_i - E_j} \tag{192}$$

Altogether, the corrections give the following energy level diagram:



Thus, we obtain a ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contribution to the exchange parameter (\mathbf{J})

$$\mathbf{J} = J_F + J_{AF} = 2k - \frac{4(\beta+1)^2}{j^0-j}. \tag{193}$$

Net ferromagnetic coupling occurs when J_F dominates, while net antiferromagnetic occurs when the J_{AF} term outweighs the J_F term. The ferromagnetic contribution is simply twice the exchange integral,

$$k = \left\langle a(1)b(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle$$

and the antiferromagnetic contribution is embodied in the configuration interaction term. Here

$$\beta = \langle a(1) | h(1) | b(1) \rangle \text{ and } l = \left\langle a(1)a(1) \left| \frac{1}{r_{12}} \right| a(2)b(2) \right\rangle$$

Remember that the exchange integral is the electron-electron repulsion in the *overlap region*. This is the amount of energy the system "saves" by aligning its electrons in a parallel, high-spin fashion. The greater the overlap region, the more stable the *triplet* state. This is the essence of Hund's Rule: place unpaired electrons into each degenerate orbital (to maximize M_s) before doubly occupying an orbital. Another way of explaining the Pauli principle: electrons of the same spin avoid each other. *Remember, that the region of space where two different electrons co-exist is the overlap region.*

Thus, when two orbitals share a common volume element, spin-aligned electrons avoid this region of shared space and experience less electron-electron repulsion. Yet another way of expressing the correlated motion of spin-aligned electrons is to examine the spatial wavefunctions that describe their motion.

$$\psi_A = \frac{1}{\sqrt{2}}(a(1)b(2) - b(1)a(2)) \quad \text{Triplet} \quad (194)$$

$$\psi_{S,OS} = \frac{1}{\sqrt{2}}(a(1)b(2) + b(1)a(2)) \quad \text{Open-shell Singlet} \quad (195)$$

When two electrons approach each other, their coordinates become nearly identical. In this case, consider the limit of each spatial wavefunction when the coordinates of electron 1 approach those of electron 2:

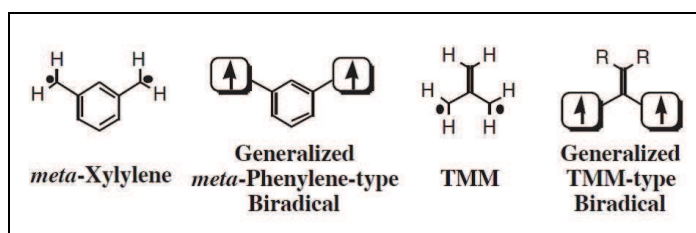
$$\lim_{\psi_-} = \lim\{0.707[\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)]\} \approx 0.707[\phi_A(2)\phi_B(2) - \phi_B(2)\phi_A(2)] = 0 \quad (196)$$

$$\lim_{\psi_+} = \lim\{0.707[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)]\} \approx 0.707[\phi_A(2)\phi_B(2) + \phi_B(2)\phi_A(2)] \neq 0 \quad (197)$$

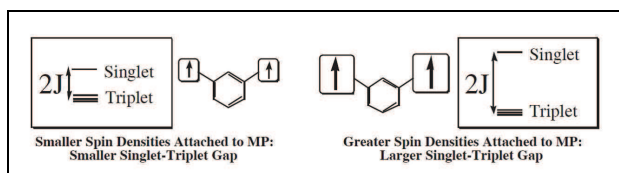
In a sense, spin-aligned electrons avoid each other to prevent the wavefunction from vanishing, while spin-paired electrons do not have to avoid each other. This is just another way to formulate the Pauli Exclusion Principle (no two electrons can have the same four quantum numbers). Of course, the result is a lower energy when

two, orthogonal, singly-occupied orbitals that share a common volume element have unpaired electrons that are spin-parallel (*i.e.*, a *triplet* state).

The discussion above gives a quantum mechanical explanation of a singlet-triplet gap. Biradicals that have degenerate or nearly isoenergetic SOMOs (Singly Occupied Molecular Orbital) and that and whose eigenvectors (coefficients) cannot be relegated to different sets of atoms are said to be nondisjoint.⁴ Such biradicals are expected to have nonzero exchange integrals and triplet ground states. Many examples of nondisjoint biradicals are meta-phenylene-type biradicals (from the parent *meta-xylene*) and trimethylenemethane (TMM)-type biradicals (from the parent trimethylenemethane).

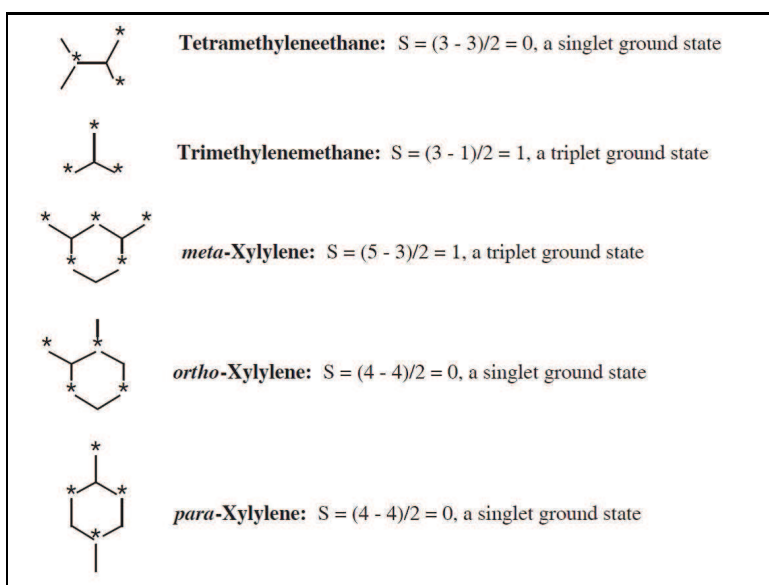
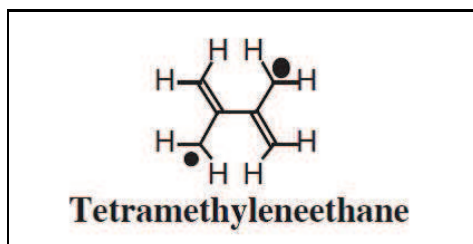


The effectiveness of a ferromagnetic coupling group is based on (1) its π -topology, (2) the spin density at the carbons attached to the coupler: the smaller the spin density, the smaller the gap ($2J$) between the ground-state triplet and the higher-energy singlet state (spin density in the coupler is directly proportional to the exchange integral); and (3) the presence of steric interactions that attenuate conjugation of the spin-containing unit with the coupler fragment.



There are many types of disjoint biradicals - those in which the coefficients of the SOMOs can be isolated on different molecular fragments. These biradicals are expected to have vanishingly small singlet-triplet gaps or singlet ground states. The most studied disjoint biradical is tetramethylethane and its derivatives.

You may recognize tetramethylethane as two allyl radicals joined at nodal C2. In fact, any biradical linked by nodal carbons is disjoint and is expected to be a singlet ground state molecule. Not surprisingly, there are topology rules for high-spin molecules. The most popular is the "star, non-star rule." It works only for even alternant systems. Star, or label alternant atoms of the biradical, such that no two starred atoms are contiguous. The ground state spin is thus, $S = (\text{star} - \text{nonstar})/2$.



8.2. Approximate approaches to the Dirac equation

back to Dirac:

Dirac equation satisfies requirements of special relativity in connection with the quantum behaviour of the electron. Special relativity refers to systems which move with a constant velocity with respect to each other

→ **not** a good approximation for the movement of an electron around a nucleus!

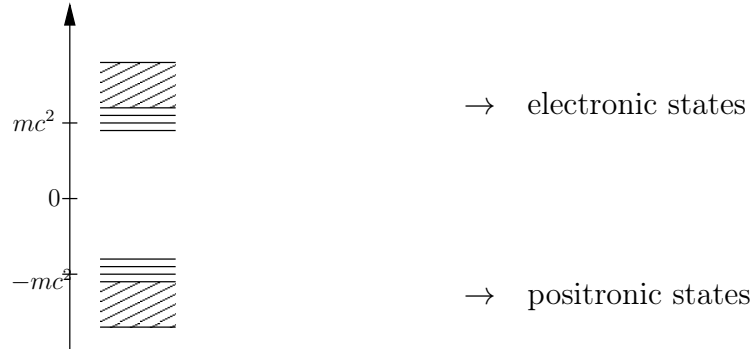
However, at present (as far as I know) no consistent theory describing the quantum aspects of gravitation available.

Dirac equation four-dimensional

→ ψ contains four components:

$$\psi = \begin{pmatrix} \psi_{L\alpha} \\ \psi_{L\beta} \\ \psi_{S\alpha} \\ \psi_{S\beta} \end{pmatrix} \left. \begin{array}{l} \} \text{large component} \\ \} \text{small component} \end{array} \right\}$$

Solutions with negative energies are interpreted as positrons:



in the presence of electric and magnetic fields the Dirac equation is modified to

$$\left\{ c\bar{\alpha} \cdot \bar{\pi} + \hat{\beta}' mc^2 + V \right\} \psi = i \frac{\partial \psi}{\partial t}$$

V : electrostatic potential

$\bar{\pi} = \bar{p} + \bar{A}$, \bar{A} : vector potential, $\bar{B} = \nabla \times \bar{A}$

rest energy normalization (in order to increase the accuracy given that the hydrogen binding energy of the order of 13.6 eV is small compared to mc^2)

$$\hat{\beta} \rightarrow \hat{\beta}' = \begin{pmatrix} 0 & 0 \\ 0 & -2I \end{pmatrix}; \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

time independent case

$$\left\{ c\bar{\alpha}\bar{\pi} + \hat{\beta}' mc^2 + V \right\} \psi = E\psi$$

can be factored out in two equations

$$\begin{aligned} c(\bar{\sigma}\bar{\pi})\psi_S + V\psi_L &= E\psi_L \\ c(\bar{\sigma}\bar{\pi})\psi_L + (-2mc^2 + V)\psi_S &= E\psi_S \end{aligned}$$

solve the latter for ψ_S

$$\psi_S = (E + 2mc^2 - V)^{-1} c(\bar{\sigma}\bar{\pi}) \psi_L$$

write

$$\begin{aligned} (E + 2mc^2 - V)^{-1} &= (2mc^2)^{-1} \left(1 + \frac{E - V}{2mc^2} \right)^{-1} \\ &= (2mc^2)^{-1} k \end{aligned}$$

$$\Rightarrow \psi_S = k \cdot \frac{\bar{\sigma}\bar{\pi}}{2mc} \psi_L$$

enter upper equation

$$\Rightarrow \left\{ \frac{1}{2m} (\bar{\sigma}\bar{\pi}) k (\bar{\sigma}\bar{\pi}) + (-E + V) \right\} \psi_L = 0$$

► non-relativistic limit ($c \rightarrow \infty$) $\Rightarrow k = 1$

► expand $\bar{\pi} = \bar{p} + \bar{A}$, $\bar{p} = -i\nabla$, $\bar{B} = \nabla \times \bar{A}$

$$\Rightarrow \left\{ \frac{\bar{\pi}^2}{2m} + V + \frac{\bar{\sigma}\bar{B}}{2m} \right\} \psi_L = E\psi_L \quad \text{where } \frac{\bar{\sigma}\bar{B}}{2m} : \text{Zeeman interaction}$$

obtain SE with extra term representing the interaction of an external magnetic field with the electron spin

\Rightarrow Spin arises in the non-relativistic limit of the Dirac equation

In the non-relativistic limit

$$\psi_S = \frac{\bar{\sigma}\bar{\pi}}{2mc} \psi_L$$

use a hydrogenic wave function

$\psi_L \sim e^{-Zr}$ and atomic units ($m = 1$)

$$\Rightarrow \psi_S = \frac{Z}{2c} \psi_L = \frac{Z}{274} \psi_L$$

i.e. for hydrogen the small component accounts for only $10^{-3}\%$ of the electron density, however, for uranium $1s$ it is about 10%

relativistic correlations from expanding the k factor

$$k = \left(1 + \frac{E - V}{2mc^2} \right)^{-1} \approx 1 - \frac{E - V}{2mc^2} + \dots$$

Pauli equation

$$\left\{ \frac{\bar{\pi}^2}{2m} + V - \frac{\bar{\pi}^4}{8m^3c^2} + \frac{Z\bar{S}\bar{L}}{2m^2c^2r^3} + \frac{Z\pi\delta(r)}{2m^2c^2} + \frac{\bar{\sigma}\bar{B}}{2m} \right\} \psi_L = E\psi_L$$

↓

mass-velocity
correction

↓

spin-orbit
term
 $\bar{L} = \bar{r} \times \bar{\pi}$

↓

Darwin
correction

The last term containing the δ function is the Darwin correction, which is often interpreted as the electron making a high-frequency oscillation around its mean position, referred to as Zitterbewegung.

problem: expansion above requires $E - V \ll 2mc^2$, this is not valid near the nucleus where $V \rightarrow -\infty$

$$\Rightarrow \text{write } (E + 2mc^2 - V)^{-1} = (2mc^2 - V)^{-1} \left(1 + \frac{E}{2mc^2 - V}\right)^{-1} \\ = (2mc^2 - V)^{-1} k'$$

$$k' = \left(1 + \frac{E}{2mc^2 - V}\right)^{-1} \approx 1 - \frac{E}{2mc^2 - V} + \dots$$

zero-order term: $k = 1$

\Rightarrow Zero-Order Regular Approximation (**ZORA**)

$$\left\{ \bar{\pi} \frac{c^2}{2m^2c^2 - V} \bar{\pi} + \left(\frac{c^2}{2m^2c^2 - V} \right) \frac{2Z\bar{S} \cdot \bar{L}}{r^3} + V \right\} \psi_L = E\psi_L$$

(spin-orbit coupling included in zero order!)

including the first order term in k'

\Rightarrow First-Order Regular Approximation (**FORA**)

Many-particle systems:

No satisfactory description available yet,
 recipes:

- ▶ assign each electron a Dirac operator ($c\bar{\alpha}\bar{\pi} + \hat{\beta}'mc^2$)
- ▶ sum these operators up
- ▶ include retardation effects (approximately) in Coulomb operator by expanding the potential in powers of $\frac{1}{c}$ up to order $\frac{1}{c^2}$, this leads to

$$V_{ee}(r_{12}) = \frac{1}{r_{12}} \rightarrow \frac{1}{r_{12}} - \frac{1}{r_{12}} \left[\bar{\alpha}_1 \bar{\alpha}_2 + \frac{(\bar{\alpha}_1 \times \bar{r}_{12})(\bar{\alpha}_2 \times \bar{r}_{12})}{2r_{12}^2} \right]$$

- one-electron operators:

$$H_e^{Zeeman} = \sum_i \left[\bar{s}_i \bar{B}_i - \frac{1}{2mc^2} (\bar{s}_i \bar{B}_i) \bar{\pi}_i^2 \right]$$

$$H_e^{mv} = -\frac{1}{8m^3c^2} \sum_i \bar{\pi}_i^4 \quad \text{mass-velocity correction}$$

due to the dependence of the electron mass on the velocity

$$H_e^{so} = -\frac{1}{4mc^2} \sum_i (\bar{s}_i \cdot \bar{\pi}_i \times \bar{F}_i - \bar{s}_i \bar{F}_i \times \bar{\pi}_i)$$

$$\downarrow$$

$$F = -\nabla\phi : \quad \text{external electric potential}$$

- and two-electron operators:

$$H_{ee}^{so} = -\frac{1}{2m^2c^2} \sum_i \sum_{j \neq i} \frac{\bar{s}_i \cdot (\bar{r}_{ij} \times \bar{\pi}_i)}{r_{ij}^3}$$

(interaction of spin with mag. field due to its own movement)

$$H_{ee}^{soo} = -\frac{1}{m^2c^2} \sum_i \sum_{j \neq i} \frac{\bar{s}_i \cdot (\bar{r}_{ij} \times \bar{\pi}_j)}{r_{ij}^3}$$

(spin-other-orbit operator, describes the interaction of an electronic spin with the mag. field generated by the movements of the other electrons)

$$H_{ee}^{ss} = \frac{1}{2c^2} \sum_i \sum_{j \neq i} \left(\frac{\bar{s}_i \cdot \bar{s}_j}{r_{ij}^3} - 3 \frac{(\bar{s}_i - i\bar{r}_{ij})(\bar{r}_{ij} \bar{s}_j)}{r_{ij}^5} \right) - \frac{8\pi}{3} \sum_{i,j} (\bar{s}_i \bar{s}_j) \delta(\bar{r}_{ij})$$

$$H_{ee}^{oo} = -\frac{1}{4m^2c^2} \sum_i \sum_{j \neq i} \left(\frac{(\bar{\pi}_i \cdot \bar{\pi}_j)}{r_{ij}} + \frac{(\bar{\pi}_i \cdot \bar{r}_{ij})(\bar{r}_{ij} \cdot \bar{\pi}_i)}{r_{ij}^3} \right)$$

$$H_{ee}^{Darwin} = -\frac{\pi}{2m^2c^2} \sum_i \sum_{j \neq i} \delta(\bar{r}_{ij})$$

- Analogous corrections arise for the nuclei. However, due to the BOA the terms with $\frac{1}{M} (\rightarrow 0)$ disappear. The only remaining terms are

$$H_n^{Zeeman} = -\mu_N \sum_A g_A \bar{I}_A \cdot \bar{B}_A \quad \bar{I}_A : \quad \text{nuclear spin}$$

$$H_{nn}^{ss} = \frac{\mu_N^2}{2c^2} \sum_A \sum_B g_A g_B \left(\frac{\bar{I}_A \cdot \bar{I}_B}{r_{AB}^3} - 3 \frac{(\bar{I}_A \cdot \bar{r}_{AB})(\bar{r}_{AB} \cdot \bar{I}_B)}{r_{AB}^5} \right)$$

(contact term $\sim \delta(\bar{r}_{AB})$ disappears, because nuclei cannot occupy the same position)

- operators involving one nucleus and one electron

$$H_{ne}^{so} = \frac{1}{2mc^2} \sum_i \sum_A Z_A \frac{\bar{s}_i(\bar{r}_{iA} \times \bar{\pi}_i)}{r_{iA}^3}$$

$$H_{ne}^{pso} = \frac{\mu_N}{mc^2} \sum_i \sum_A g_A \frac{\bar{I}_A(\bar{r}_{iA} \times \bar{\pi}_i)}{r_{iA}^3}$$

(paramagnetic-spin-orbit operator)

$$H_{ne}^{ss} = -\frac{\mu_N}{c^2} \sum_i \sum_A g_A \left(\frac{\bar{s}_i \bar{I}_A}{r_{iA}^3} - 3 \frac{(\bar{s}_i \bar{r}_{iA})(\bar{r}_{iA} \bar{I}_A)}{r_{iA}^5} + \frac{8\pi}{3} (\bar{s}_i \bar{I}_A) \delta(r_{iA}) \right)$$

$$H_{ne}^{Darwin} = \frac{\pi}{2m^2 c^2} \sum_i \sum_A Z_A \delta(\bar{r}_{iA})$$

Summary of influence of relativistic effects

- (i) difference in the dynamics due to velocity-dependent mass of the electrons
→ alters size of the orbitals
- (ii) magnetic interactions due to spin
→ destroys the picture of an orbital having a definite spin
- (iii) positron (i.e., negative energy) states coupling between electronic and positronic states introduces a "small" component in the electronic wave function
→ shape of the orbitals changes
(relativistic wave functions do not have nodes)
- (iv) retardation of the potential

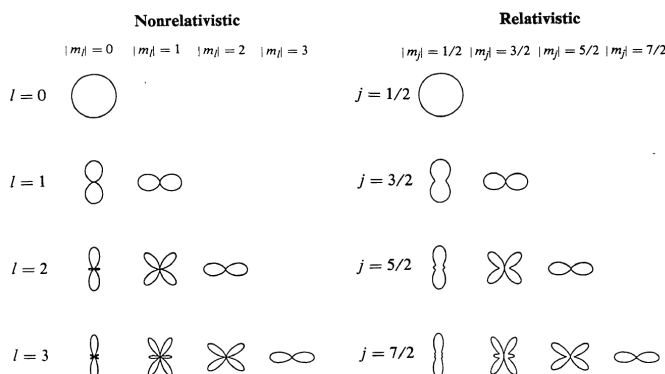
Example: Orbitals

Fig. 2. Polar diagrams of squared angular wavefunctions ('orbital shapes').

[*KG Dyall, Inclusion of Relativistic Effects in Electronic Structure Calculations, Austral. J. Physics* **39**, 667 (1986)]

Examples:

HF-level calculations with and without relativistic corrections from *Pisani & Clementi, J. Chem. Phys.* **101**, 3079 (1994)

| | | E | $R_{eq}/\text{\AA}$ | θ |
|---------|----------|-----------|---------------------|----------|
| H_2O | non-rel. | -76.05 | 0.94 | 107.75 |
| | rel. | -76.11 | 0.94 | 107.68 |
| H_2S | non-rel. | -398.64 | 1.34 | 94.23 |
| | rel. | -399.75 | 1.34 | 94.14 |
| H_2Se | non-rel. | -2400.98 | 1.45 | 93.14 |
| | rel. | -2429.61 | 1.45 | 92.87 |
| H_2Te | non-rel. | -6612.80 | 1.66 | 92.57 |
| | rel. | -6794.87 | 1.65 | 91.99 |
| H_2Po | non-rel. | -20676.71 | 1.75 | 92.21 |
| | rel. | -22232.53 | 1.74 | 90.59 |

\Rightarrow relativistic effects become comparable to those from electron correlation and basis set for $Z \gtrsim 40$

Relativistic methods that include electron effects analogous to CI, MCSCF, MP & CC are presently at development stage.

9. Semi-Empirical Methods

In chapter 3.3 the HF approximations has been introduced, in 4 & 6 we tried to improve upon that introducing electron correlation.

There exists, however, many frequently used methods which are derived from HF by simplifying the equations.

Reminder HF equations:

$$\hat{F}_i \phi_i = \varepsilon_i \phi_i$$

with Fock operator

$$\hat{F}_i = \hat{h}_i + \sum_j^N (\hat{J}_j - \hat{k}_j)$$

with Coulomb-operator

$$\hat{J}_i |\phi_j(2)\rangle = \langle \phi_i(1) | \frac{1}{|r_1 - r_2|} | \phi_i(1)\rangle | \phi_j(2)\rangle$$

and exchange operator

$$\hat{k}_i |\phi_j(2)\rangle = \langle \phi_i(1) | \frac{1}{|r_1 - r_2|} | \phi_j(1)\rangle | \phi_i(2)\rangle$$

↑
exchange!

expand MOs in terms of basis functions centered at atoms, conventionally called atomic orbitals (LCAO: Linear Combination of Atomic Orbitals), although they are generally not solutions to the atomic HF problem

$$\phi_i = \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha}$$


⇒ write HF equations as


$$\hat{F}_i \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha} = \varepsilon_i \sum_{\alpha}^M c_{\alpha i} \chi_{\alpha}$$

apply $\int \chi_{\beta}(r) d^3\bar{r}$

⇒

| |
|---|
| Roothan-Hall equations $FC = SC\varepsilon$ |
|---|


 Fock matrix


 overlap matrix

$$\begin{aligned}
 \langle \chi_\alpha | \hat{F} | \chi_\beta \rangle &= \langle \chi_\alpha | \hat{h} | \chi_\beta \rangle + \sum_j^{occ} \langle \chi_\alpha | J_j - k_j | \chi_\beta \rangle \\
 &= h_{\alpha\beta} + \sum_j^{occ} \left\{ \langle \chi_\alpha \phi_j | \frac{1}{r_{12}} | \chi_\beta \phi_j \rangle \right. \\
 &\quad \left. - \langle \chi_\alpha \phi_j | \frac{1}{r_{12}} | \phi_j \chi_\beta \rangle \right\} \\
 &= h_{\alpha\beta} + \sum_j^{occ} \sum_\gamma^{AO} \sum_\sigma^{AO} c_{\gamma j} c_{\sigma j} \\
 &\quad \times \left(\langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\beta \chi_\sigma \rangle - \langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\sigma \chi_\beta \rangle \right) \\
 &\Rightarrow F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\sigma} G_{\alpha\beta\gamma\sigma} D_{\gamma\sigma} \\
 \text{where } D_{\gamma\sigma} &= \sum_j^{occ} c_{\gamma j} c_{\sigma j} \\
 \text{and } G_{\alpha\beta\gamma\sigma} &= \left(\langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\beta \chi_\sigma \rangle \right. \\
 &\quad \left. - \langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\sigma \chi_\beta \rangle \right)
 \end{aligned}$$

The idea of semi-empirical methods consists in neglecting some wave function and parameterizing some of the integrals. In detail:

► **Neglect of Diatomic Differential Overlap Approximation (NDDO)**

neglect all products of basis functions depending on the same electron coordinate when located on different atoms:

μ_A : orbitals on centre A

ν_B : orbitals on centre B

$$\Rightarrow \mu_A(i) \nu_B(i) = 0$$

(i) $S_{\mu\nu} = \langle \mu_A | \nu_B \rangle = \delta_{\mu\nu} \delta_{AB}$

μ : s -type orbital

ν : p -type orbital

(ii) one-electron integrals

$$\begin{aligned}
 \langle \mu_A | h | \nu_A \rangle &= \langle \mu_A | -\frac{\nabla^2}{2} - V_A | \nu_A \rangle \\
 &\quad - \sum_{B \neq A} \langle \mu_A | V_B | \nu_A \rangle \\
 \langle \mu_A | h | \nu_B \rangle &= \langle \mu_A | -\frac{\nabla^2}{2} - V_A - V_B | \nu_B \rangle \\
 \langle \mu_A | V_C | \nu_B \rangle &= 0
 \end{aligned}$$

(iii) two-electron integrals

$$\langle \mu_A \nu_B | \frac{1}{r_{12}} | \lambda_C \sigma_D \rangle = \delta_{AC} \delta_{BD} \langle \mu_A \nu_B | \frac{1}{r_{12}} | \chi_A \sigma_B \rangle$$

► **Intermediate Neglect of Differential Overlap (INDO)**

involves the following additional approximations, besides those for NDDO

$$\begin{aligned}
 \langle \mu_A | h | \nu_A \rangle &= -\delta_{\mu\nu} \sum_B \underbrace{\langle \mu_A | V_B | \mu_A \rangle}_{\substack{\text{parameter independent} \\ \text{of orbitals type} \\ (s \text{ or } p)}} \\
 \langle \mu_A \nu_B | \frac{1}{r_{12}} | \lambda_C \sigma_D \rangle &= \delta_{\mu_A \lambda_C} \delta_{\nu_B \sigma_D} \underbrace{\langle \mu_A \nu_B | \frac{1}{r_{12}} | \mu_A \nu_B \rangle}
 \end{aligned}$$

► **Complete Neglect of Differential Overlap (CNDO)**

even more drastic approximations compared to NDDO/INDO, only the Coulomb one-centre and two-centre two-electron integrals remain:

$$\begin{aligned}
 \langle \mu_A \nu_B | \frac{1}{r_{12}} | \lambda_C \sigma_D \rangle &= \delta_{AC} \delta_{BD} \delta_{\mu\nu} \delta_{\nu\sigma} \\
 &\quad \times \underbrace{\langle \mu_A \nu_B | \frac{1}{r_{12}} | \mu_A \nu_B \rangle}_{\substack{\text{parameters independent} \\ \text{of orbital type} \\ (\gamma_{AA}, \gamma_{AB})}}
 \end{aligned}$$

approximations for one-electron integrals are the same as for INDO

► **Pariser-Pople-Parr (PPP) method**

≙ CNDO, but only π -electrons are considered

The methods above can be further classified according to their parameterization

MINDO/1, MINDO/2 and MINDO/3 are modifications of INDO (Modified Intermediate Neglect of Differential Overlap)

MINDO/3 quite widely used

[Steward, *Rev. Comput. Chem.* **1**, 45 (1990)]

here

$$\langle \mu_A | h | \nu_B \rangle = \langle \mu_A | \nu_B \rangle \beta_{AB} (I_\mu + I_\nu)$$

\nearrow
 parameters

\searrow
 ionization
 potentials

MINDO, AM1, PM3 are parameterizations of the NDDO



Parametric Method No. 3

parameterization for many combinations of atoms

[Steward, *J. Comput. Chem.* **10**, 209 (1989)]

Austin Model 1

(in honour of Dewar's move to the University of Austin)

[Dewar et al. *J. Am. Chem. Soc.* **107**, 3902 (1985)]

Modified Neglect of Differential Overlap

[Dewar & Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977)]

Accuracy?

| | MNDO | AM1 | PM |
|------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| average error in bond angles | 4.3° | 3.3° | 3.9° |
| average error in bonds to H | 0.015 Å | 0.006 Å | 0.005 Å |
| C | 0.002 | 0.002 | 0.002 |
| N | 0.015 | 0.014 | 0.012 |
| O | 0.017 | 0.011 | 0.006 |
| Si | 0.030 | 0.019 | 0.045 |
| average error in ionization pot. | 0.78 eV | 0.61 eV | 0.57 eV |
| average error in dipole moment | 0.45 D | 0.35 D | 0.38 D |
| average error in heat of formation | 46.2 $\frac{\text{kcal}}{\text{mol}}$ | 27.6 $\frac{\text{kcal}}{\text{mol}}$ | 11.6 $\frac{\text{kcal}}{\text{mol}}$ |

► **Extended Hückel Theory (EHT)**

[Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963)]

parameterization of the Fock matrix elements using atomic ionization potentials:

$$F_{\mu\mu} = -I_{\mu}$$

$$F_{\mu\nu} = -k \left(\frac{I_{\mu} + I_{\nu}}{2} \right) S_{\mu\nu}; \quad k \approx 1.75$$

► **Simple Hückel Theory**

approximations are taken to the limit, only planar conjugated systems are considered, σ -orbitals are neglected, F matrix for π -electrons:

$$F_{\mu_A\mu_A} = \alpha_A$$

$$F_{\mu_A\mu_B} = \begin{cases} \beta_{AB} & (A \text{ and } B \text{ are neighbours}) \\ 0 & (A \text{ and } B \text{ are not neighbours}) \end{cases}$$

α_A and β_{AB} are parameters that depend on the "atom type" (i.e. nuclear charge and bonding situation), similar to force field methods

Extended and simple Hückel methods are mainly used for educational purposes or for producing an electronic starting configuration for a more refined SCF technique.

10. Appendix

10.1. Linear-response theory

Consider a quantum mechanical observable $\hat{\alpha}$ whose ground state expectation value is given by

$$\alpha_0 = \langle \psi_0 | \hat{\alpha} | \psi_0 \rangle$$

where $|\psi_0\rangle$ is the ground-state many-body wave function associated with the static Hamiltonian \hat{H}_0 . Now assume that the system is acted upon by a time-dependent perturbation.

$$\hat{H}_1(t) = F(t)\hat{\beta} \quad t \geq t_0$$

where $F(t)$ is an external field that couples to an observable $\hat{\beta}$ and which is switched on at a time t_0 . This perturbation affects the wave function of the system and thus the expectation value of the observable α , which now becomes time-dependent

$$\alpha(t) = \langle \psi(t) | \hat{\alpha} | \psi(t) \rangle$$

The difference between the time-dependent expectation value of $\hat{\alpha}$ and its initial value α_0 is called the response of $\hat{\alpha}$ to the perturbation. Expand the response in powers of the field $F(t)$

$$\alpha(t) - \alpha_0 = \alpha_1(t) + \alpha_2(t) + \dots$$

\uparrow
 linear
 response

\nwarrow
 quadratic
 response

to calculate $\alpha_1(t)$ we change into the interaction representation

$$\begin{aligned} |\psi_I(t)\rangle &= e^{i\hat{H}_0 t} |\psi(t)\rangle \\ |\psi(t)\rangle &= e^{-i\hat{H}_0 t} |\psi_I(t)\rangle \\ i\frac{\partial}{\partial t} |\psi\rangle &= \{\hat{H}_0 + \hat{H}_1\} |\psi(t)\rangle \\ \hat{H}_0 e^{-i\hat{H}_0 t} |\psi_I\rangle + i e^{-i\hat{H}_0 t} \frac{\partial}{\partial t} |\psi_I\rangle &= \{\hat{H}_0 + \hat{H}_1\} e^{-i\hat{H}_0 t} |\psi_I\rangle \\ \Rightarrow i\frac{\partial}{\partial t} |\psi_I(t)\rangle &= \underbrace{e^{i\hat{H}_0 t} \hat{H}_1 e^{-i\hat{H}_0 t}}_{\hat{H}_{1I}} |\psi_I(t)\rangle \end{aligned}$$

Thus the interaction state Ket evolves according to the dynamics governed by \hat{H}_{1I}

$$|\psi_I(t)\rangle = |\psi_0\rangle - i \int^t dt' \hat{H}_{1I}(t') |\psi_I(t')\rangle$$

iterative solution

$$|\psi_I(t)\rangle \approx |\psi_0\rangle - i \int^t dt' \hat{H}_{1I}(t') |\psi_0\rangle$$

$$\alpha(t) = \langle \psi(t) | \hat{\alpha}(t) | \psi(t) \rangle = \langle \psi_I(t) | \hat{\alpha}_I(t) | \psi_I(t) \rangle$$

for evaluation of the matrix element we use

$$\langle \psi_I(t) | \approx \langle \psi_0 | + i \int^t dt' \langle \psi_0 | \hat{H}_{1I}(t')$$

and obtain

$$\begin{aligned} \alpha(t) &= \overbrace{\langle \psi(t) | \hat{\alpha}_I | \psi_0 \rangle}^{\alpha_0} + i \int^f dt' \langle \psi_0 | \hat{H}_{1I} \hat{\alpha}_I | \psi_0 \rangle - i \int^f dt' \langle \psi_0 | \hat{\alpha}_I \hat{H}_{1I} | \psi_0 \rangle + \mathcal{O}(\hat{H}_{1I}^2) \\ &\rightarrow \text{neglected for linear response} \end{aligned}$$

$$\alpha_1 = \alpha(t) - \alpha_0 \approx -i \int^t dt' F(t') \langle \psi_0 | [\hat{\alpha}_I(t), \hat{\beta}_I(t')] | \psi_0 \rangle$$

Since the initial-state Hamiltonian \hat{H}_0 is time-independent, we can replace the commutator $[\hat{\alpha}_I(t), \hat{\beta}_I(t')]$ with $[\hat{\alpha}_I(t-t'), \hat{\beta}_I]$ in the equation above. We define the retarded response function

$$\chi_{\alpha\beta}(t-t') = -i\Theta(t-t') \langle \psi_0 | [\hat{\alpha}_I(t-t'), \hat{\beta}_I] | \psi_0 \rangle$$

and obtain the linear response

$$\alpha_1(t) = \int_{-\infty}^{\infty} dt' \chi_{\alpha\beta}(t-t') F(t')$$

The linear-response function in frequency space follows as

$$\alpha_1(\omega) = \chi_{\alpha\beta}(\omega) F(\omega)$$

where

$$\chi_{\alpha\beta}(\omega) = -i \int_{-\infty}^{\infty} d\tau \Theta(\tau) \langle \psi_0 | [\hat{\alpha}_I(\tau), \hat{\beta}] | \psi_0 \rangle e^{i\omega\tau}$$

Now use $1 = \sum_{-\infty}^{\infty} |\psi_n \rangle \langle \psi_n|$ where $\{|\psi_n \rangle\}$ is the complete set of eigen functions of \hat{H}_0 , i.e., $\hat{H}_0 |\psi_n \rangle = E_n |\psi_n \rangle$

$$\begin{aligned} \chi_{\alpha\beta}(\omega) = & -i \sum_{n=0}^{\infty} \int d\tau \Theta(\tau) e^{i\omega\tau} \times \\ & \left\{ \underbrace{\langle \psi_0 | \hat{\alpha}_I(\tau) | \psi_n \rangle}_{\langle \psi_0 | e^{i\hat{H}_0\tau} \hat{\alpha} e^{-i\hat{H}_0\tau} | \psi_n \rangle} \underbrace{\langle \psi_n | \hat{\beta} | \psi_0 \rangle}_{\langle \psi_n | e^{i\hat{H}_0\tau} \hat{\beta} e^{-i\hat{H}_0\tau} | \psi_0 \rangle} - \underbrace{\langle \psi_0 | \hat{\beta} | \psi_n \rangle}_{\langle \psi_0 | \hat{\beta} | \psi_n \rangle} \underbrace{\langle \psi_n | \hat{\alpha}_I(\tau) | \psi_0 \rangle}_{\langle \psi_n | e^{i\hat{H}_0\tau} \hat{\alpha} e^{-i\hat{H}_0\tau} | \psi_0 \rangle} \right\} \\ & \underbrace{\langle \psi_0 | \hat{\alpha} | \psi_n \rangle e^{-i(E_n - E_0)\tau}}_{\Omega_n} \underbrace{\langle \psi_n | \hat{\alpha} | \psi_0 \rangle e^{-i(E_n - E_0)\tau}}_{\Omega_n} \end{aligned}$$

thus

$$\chi_{\alpha\beta}(\omega) = -i \sum_{n=1}^{\infty} \int d\tau \Theta(\tau) e^{i\omega\tau} \left\{ \langle \psi_0 | \hat{\alpha} | \psi_n \rangle \langle \psi_n | \hat{\beta} | \psi_0 \rangle e^{-i\Omega_n\tau} - \langle \psi_0 | \hat{\beta} | \psi_n \rangle \langle \psi_n | \hat{\alpha} | \psi_0 \rangle e^{i\Omega_n\tau} \right\}$$

Next we use the integral representation of the step function

$$\Theta(\tau) = \lim_{\eta \rightarrow 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{e^{i\omega'\tau}}{\omega' + i\eta}$$

together with the general relation

$$\int_{-\infty}^{\infty} dt' e^{it'(\omega - \omega')} = 2\pi \delta(\omega - \omega')$$

and obtain the

Lehmann presentation of the linear response function

$$\chi_{\alpha\beta}(\omega) = \lim_{\eta \rightarrow 0^+} \sum_{n=1}^{\infty} \left\{ \frac{\langle \psi_0 | \hat{\alpha} | \psi_n \rangle \langle \psi_n | \hat{\beta} | \psi_0 \rangle}{\omega - \Omega_n + i\eta} - \frac{\langle \psi_0 | \hat{\beta} | \psi_n \rangle \langle \psi_n | \hat{\alpha} | \psi_0 \rangle}{\omega + \Omega_n + i\eta} \right\}$$

It shows how a frequency-dependent perturbation couples to the excitation spectrum $\Omega_n = E_n - E_0$ of the system.

Example: Photoresponse in linear response

Consider external perturbation associated with a monochromatic electric field along z

$$v_1(r, t) = E \cdot z \cdot \sin(\omega t)$$

induces a density response

$$n_1(r, \omega) = \int dr' \chi_{nn}(r, r', \omega) v_1(r', \omega)$$

which gives rise to a dipole polarizability

$$p_{1z} = - \int dr z \cdot n_1(r)$$

Using $p_1(\omega) = \alpha(\omega)E(\omega)$

One thus obtains the dynamic polarizability

$$\alpha_{zz} = \sum_{n=1}^{\infty} \left\{ \frac{|\langle \psi_n | \hat{z} | \psi_0 \rangle|^2}{\omega - \Omega_n + i\eta} - \frac{|\langle \psi_n | \hat{z} | \psi_0 \rangle|^2}{\omega + \Omega_n + i\eta} \right\}$$

which corresponds to Fermi's Golden Rule

10.2. Functionals and functional derivations

Consider a space Φ spanned by a set of functions φ of n real variables

$$\Phi = \{\varphi : \mathbb{R}^n \rightarrow \mathbb{R}\}$$

The map $F : \Phi \rightarrow \mathbb{R}$ (or \mathbb{C}) is called a functional. In other words, every φ from the space of functions is mapped into a real (or complex) number

$$\varphi(x) \rightarrow F[\varphi]$$

We follow here the conventional notation which puts the argument of the functional F in square brackets. Note that the functions φ itself does not need to be given with an argument: $F[\varphi(x)]$ and $F[\varphi(y)]$ mean the same thing, therefore we should better drop x and y altogether.

In DFT, we often encounter functionals (such as the xc functional) which also depend explicitly on a spatial coordinate. In this case we use the notation $F[\varphi](y)$. This simply means that F is at each point y , a functional of φ .

Examples:

- $F_1[\varphi] = \int_a^b dx \varphi(x)$

Here the functional is given by a definite integral over some function φ .

- $F_2[\varphi] = \varphi(x_0)$

Here the functional is given by evaluating the function φ at a fixed point

- $I[q] = \int_{t_1}^{t_2} dt L(q(t), \frac{dq(t)}{dt})$

is the well-known action functional known from classical physics.

Let us now define the functional derivative as follows

$$\frac{\delta F[\varphi]}{\delta \varphi(y)} = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \{F[\varphi(x) + \epsilon \delta(x - y)] - F[\varphi(x)]\}$$

Note that for a fixed $y = y_0$ the derivative of a functional is again a functional. On the other hand, one is usually interested in the functional derivative for variable y . In that case the functional derivative becomes a function of y .

Examples:

- $F[\varphi] = \varphi(x)$

$$\frac{\delta F[\varphi]}{\delta \varphi(y)} = \frac{\delta \varphi(x)}{\delta \varphi(y)} = \delta(x - y)$$

- $F[\varphi] = \varphi^2(x) = \varphi(x)\varphi(x)$

$$\begin{aligned} \frac{\delta \varphi^2(x)}{\delta \varphi(y)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \{(\varphi(x) + \epsilon \delta(x - y))(\varphi(x) + \epsilon \delta(x - y)) - \varphi^2(x)\} \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \{2\epsilon \varphi(x) \delta(x - y) + \epsilon^2 \delta^2(x - y)\} \\ &= 2\varphi(x) \delta(x - y) \end{aligned}$$

generally it holds

$$\frac{\delta \varphi^p(x)}{\delta \varphi(y)} = p\varphi^{p-1}(x) \delta(x - y)$$

- $F[\varphi] = \int A(x) \varphi(x) dx$

$$\begin{aligned} \frac{\delta F[\varphi]}{\delta \varphi(y)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \int \{A(x)(\varphi(x) + \epsilon \delta(x - y)) - A(x)\varphi(x)\} dx \\ &= \lim_{\epsilon \rightarrow 0} \frac{\epsilon}{\epsilon} \int A(x) \delta(x - y) dx = A(y) \end{aligned}$$

- $F[\varphi] = \int dx \varphi^2(x)$

$$\begin{aligned} \frac{\delta F[\varphi]}{\delta \varphi(y)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \int dx \{(\varphi(x) + \epsilon \delta(x-y))^2 - \varphi^2(x)\} \\ &= \int dx 2\varphi(x) \delta(x-y) = 2\varphi(y) \end{aligned}$$

generally it holds

$$F[\varphi] = \int dx \varphi^p(x) \rightarrow \frac{\delta F}{\delta \varphi(y)} = p\varphi^{p-1}(y)$$

and

$$F[\varphi] = \int dx f(\varphi(x)) \rightarrow \frac{\delta F}{\delta \varphi(y)} = f'(\varphi(y))$$

- $F[\varphi] = \int dx (\nabla_x \varphi(x))^2$

$$\begin{aligned} \frac{\delta F[\varphi]}{\delta \varphi(y)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \int dx \{(\nabla_x \varphi(x) + \epsilon \nabla_x \delta(x-y))^2 - (\nabla_x \varphi(x))^2\} \\ &= 2 \int dx (\nabla_x \varphi(x)) (\nabla_x \delta(x-y)) \\ &= -2 \nabla_y^2 \varphi(y) \end{aligned}$$

important rules are the product rule

$$\frac{\delta(F_1[\varphi]F_2[\varphi])}{\delta \varphi(y)} = F_1[\varphi] \frac{\delta F_2[\varphi]}{\delta \varphi(y)} + \frac{\delta F_1[\varphi]}{\delta \varphi(y)} F_2[\varphi]$$

and the chain rule

$$\frac{\delta(F[\gamma[\varphi]])}{\delta \varphi(y)} = \int dy' \frac{\delta F[\gamma]}{\delta \gamma(y')} \frac{\delta \gamma(y')}{\delta \varphi(y)}$$

that applies when the argument γ of a functional $F[\gamma]$ is itself a functional at each point x , i.e., $\gamma[\varphi](x)$.

10.3. Acronyms

| | |
|---------|--|
| 6-12 | The inverse power dependence of Lennard–Jones terms |
| AA | All-atom (as opposed to united-atom) |
| ACM | Adiabatic connection method |
| ADF | Amsterdam density functional code |
| AIM | Atoms in molecules |
| ALDA | Adiabatic local-density approximation |
| AM1 | Austin Model 1 |
| AMBER | Assisted model building with energy refinement |
| AO | Atomic orbital |
| AOC | AM1/OPLS/CM1 |
| B | Becke (1988) exchange functional |
| B1B95 | ACM one-parameter functional |
| B3LYP | ACM using B exchange and LYP correlation functionals |
| B3PW91 | ACM using B exchange and PW91 correlation functionals |
| B86 | Becke (1986) exchange functional |
| B95 | Becke correlation functional |
| BAC | Bond-additivity correction |
| BD | CCD using Brueckner orbitals |
| BH&H | Becke half-and-half exchange functional |
| BKO | Born–Kirkwood–Onsager |
| BLYP | B exchange and LYP correlation functionals |
| BPW91 | B exchange and PW91 correlation functionals |
| BSSE | Basis set superposition error |
| CAM(B) | Cambridge modification of Becke exchange functional |
| CAS | Complete active space |
| CASPT2 | Complete active space second-order perturbation theory |
| CASSCF | Complete active space self-consistent field |
| CBS | Complete basis set |
| CCD | Coupled cluster with double substitution operator |
| CCSD | Coupled cluster with single and double substitution operators |
| CCSD(T) | CCSD with perturbative estimate for connected triples |
| CCSDT | Coupled cluster with single, double, and triple substitution operators |
| CCSDTQ | Coupled cluster including single through quadruple excitations |
| CFF | Consistent force fields |
| CHARMM | Chemistry at Harvard molecular mechanics |
| CHELP | Charges from electrostatic potentials |
| CI | Configuration interaction |
| CID | CI including only double electronic excitations |
| CIS | CI including only single electronic excitations |
| CISD | CI including single and double electronic excitations |

| | |
|---------|---|
| CIS(D) | CIS including a correction for double excitations |
| CISDT | CI including single, double and triple electronic excitations |
| CISDTQ | CI including single through quadruple electronic excitations |
| CISD(Q) | CISD with Langhoff–Davidson estimate for quadruples |
| CM1 | Charge Model 1 |
| CM2 | Charge Model 2 |
| CNDO | Complete neglect of differential overlap |
| COSMIC | Computation and structural manipulation in chemistry |
| COSMO | Conductor-like screening model |
| CP | Counterpoise; Car–Parrinello |
| C-PCM | Conductor formulation of PCM |
| CSF | Configuration state function |
| CVFF | Consistent valence force field |
| DFT | Density functional theory |
| D-PCM | Dielectric formulation of PCM |
| DZ | Double zeta (basis set) |
| DZP | Double zeta polarized (basis set) |
| EA | Electron affinity |
| ECEPP | Empirical conformational energy program for peptides |
| ECP | Effective core potential |
| EDF1 | Empirical density functional 1 |
| EFP | Effective fragment potential |
| EHT | Extended Hückel theory |
| EOM | Equation of motion |
| EPR | Electron paramagnetic resonance |
| ESFF | Extensible systematic force field |
| ESP | Electrostatic potential; Equilibrium solvation path |
| ESR | Electron spin resonance |
| EVB | Empirical valence bond |
| FDPB | Finite difference Poisson–Boltzmann |
| FEP | Free energy perturbation |
| FLOGO | Floating Gaussian orbitals |
| FT97 | Filatov and Thiel (1997) density functional |
| GAPT | Generalized atomic polar tensor |
| GB | Generalized Born |
| GGA | Generalized gradient approximation |
| GHO | Generalized hybrid orbital |
| GIAO | Gauge-including atomic orbital |
| GROMOS | Gröningen molecular simulation |

| | |
|----------|---|
| GTO | Gaussian-type orbital |
| GUI | Graphical user interface |
| GVB | Generalized valence bond |
| H&H | Half-and-half adiabatic connection formula |
| HF | Hartree–Fock |
| h.f.s | Hyperfine splitting |
| HOMO | Highest occupied molecular orbital |
| IEF | Integral equation formalism |
| IGLO | Individual gauge for localized orbitals |
| IMOMM | Integrated molecular orbital molecular mechanics |
| IMOMO | Integrated molecular orbital molecular orbital |
| INDO | Intermediate neglect of differential overlap |
| INDO/S | INDO parameterized for spectroscopy |
| IP | Ionization potential |
| IPCM | PCM with a gas-phase isodensity surface as the cavity surface |
| IR | Infrared |
| IRC | Intrinsic reaction coordinate |
| KIE | Kinetic isotope effect |
| KS | Kohn–Sham |
| LANL | Los Alamos National Laboratory |
| LCAO | Linear combination of atomic orbitals |
| LD | Langevin dipole |
| LDA | Local density approximation |
| LG | Lacks-Gordon density functional |
| LJ | Lennard–Jones |
| LMP2 | Localized MP2 |
| LSCF | Localized self-consistent field |
| LSDA | Local spin density approximation |
| LYP | Lee–Yang–Parr correlation functions |
| LUMO | Lowest unoccupied molecular orbital |
| MBPT n | Many-body perturbation theory of order n |
| MC | Monte Carlo |
| MCPF | Modified coupled-pair functional |
| MCSCF | Multiconfiguration self-consistent field |
| MD | Molecular dynamics |
| MEP | Minimum energy path; Molecular electrostatic potential |
| MINDO/3 | Modified intermediate neglect of differential overlap (version 3) |
| MM | Molecular mechanics |
| MMFF | Merck molecular force field |

| | |
|-------------|---|
| MNDO | Modified neglect of differential overlap |
| MNDOC | MNDO including electron correlation effects |
| MNDO/d | MNDO augmented with d functions for some atoms |
| MO | Molecular orbital |
| MP4SDQ | MP4 including single, double and quadruple excitations |
| MP n | Møller–Plesset perturbation theory of order n |
| m PW | Modified Perdew–Wang density functional |
| MPW1K | m PW1PW91 optimized for kinetics |
| m PW1PW91 | One-parameter ACM using PW91 functionals |
| MRCI | Multireference CI |
| MRCISD | Multireference CI including single and double excitations |
| MST | Miertus–Scrocco–Tomasi (polarized continuum) model |
| MST-ST | MST model augmented with atomic surface tensions |
| μ TST | Microcanonical transition state theory |
| μ VTST | Microcanonical variational transition state theory |
| NAO | Natural atomic orbital |
| NBO | Natural bond orbital |
| NDDO | Neglect of diatomic differential overlap |
| NMR | Nuclear magnetic resonance |
| NPA | Natural population analysis |
| ONIOM | Our own n -layered integrated molecular orbital molecular mechanics |
| o.o.p. | Out-of-plane |
| OPLS | Optimized potentials for liquid simulations |
| P | Perdew exchange functional |
| P86 | Perdew correlation functional |
| PA | Proton affinity |
| PB | Poisson–Boltzmann |
| PBC | Periodic boundary condition |
| PBE | Perdew, Burke and Enzerhof functional |
| PCM | Polarized continuum model |
| PD | Pairwise descreening |
| PDFT | Projected density functional theory |
| PEG | Polyethyleneglycol |
| PES | Potential energy surface |
| PM3 | Parameterized (NDDO) model 3 |
| PM3(tm) | PM3 with a d orbital extension to transition metals |
| PME | Particle-mesh Ewald |
| PMF | Potential of mean force |
| PMP n | Projected Møller–Plesset theory of order n |
| POS | Points on a sphere |

| | |
|----------|---|
| PP | Perfect pairing |
| PPP | Pariser–Parr–Pople |
| PUHF | Projected UHF |
| PW | Perdew–Wang (1991) exchange functional |
| PW91 | Perdew–Wang (1991) correlation functional |
| QCISD | Quadratic configuration interaction including singles and doubles |
| QCISD(T) | QCISD with perturbative estimate for connected triples |
| QM | Quantum mechanics |
| QMHO | Quantum mechanical harmonic oscillator |
| QM/MM | Quantum mechanics/molecular mechanics hybrid |
| QSPR | Quantitative structure–property relationship |
| RAS | Restricted active space |
| r.d.f. | Radial distribution function |
| RESP | Restrained ESP |
| RHF | Restricted Hartree–Fock |
| RISM | Reference interaction site model |
| RMS | Root mean square |
| RMSD | Root-mean-square deviation |
| ROHF | Restricted open-shell Hartree–Fock |
| ROKS | Restricted open-shell Kohn–Sham theory |
| ROSS | Restricted open-shell singlet density functional theory |
| RPA | Random-phase approximation |
| RRKM | Rice–Ramsperger–Kassel–Marcus |
| S | Slater exchange functional |
| SAC | Scaling all correlation |
| SAM1 | Semi- <i>ab initio</i> method 1 |
| SAM1D | SAM1 with d orbitals |
| SAR | Structure–activity relationship |
| SASA | Solvent-accessible surface area |
| SCF | Self-consistent field |
| SCIPCM | PCM with a liquid-solution-phase isodensity surface as the cavity surface |
| SCRf | Self-consistent reaction field |
| SES | Separable equilibrium solvation |
| SINDO1 | Symmetric orthogonalized INDO model |
| SMA | Small-matrix approximation |
| SM x | Solvation model x (using Cramer–Truhlar GB formalism) |
| SOMO | Singly occupied molecular orbital |
| SPA | Single-pole approximation |
| SPC | Simple point charge |
| SRP | Specific reaction (or range) parameters |

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|-----------|---|
| S–T | Singlet–triplet |
| STO | Slater-type orbital |
| TCSCF | Two-configuration self-consistent field |
| TDA | Tamm-Dancoff approximation |
| TDDFT | Time-dependent density functional theory |
| TI | Thermodynamic integration |
| TIP n P | Transferable intermolecular potentials n point charge water model |
| TMM | Trimethylenemethane |
| TS | Transition state |
| TST | Transition-state theory |
| TZ | Triple zeta (basis set) |
| TZP | Triple zeta polarized (basis set) |
| UA | United atom (as opposed to all-atom) |
| UFF | Universal force field |
| UHF | Unrestricted Hartree–Fock |
| UV | Ultraviolet |
| UV/Vis | Ultraviolet/visible |
| VB | Valence bond |
| VSEPR | Valence-shell electron-pair repulsion |
| VSIP | Valence-shell ionization potential |
| VSXC | Exchange-correlation functional of van Voorhis and Scuseria |
| VTST | Variational transition-state theory |
| VWN | A Vosko, Wilk, Nusair correlation functional |
| VWN5 | A Vosko, Wilk, Nusair correlation functional |
| XSOL | Extended RISM and quantum mechanical solvation model |
| ZPVE | Zero-point vibrational energy |