

Chemická struktura B

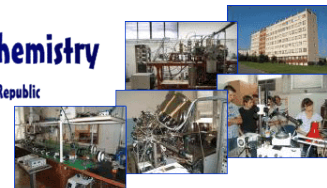
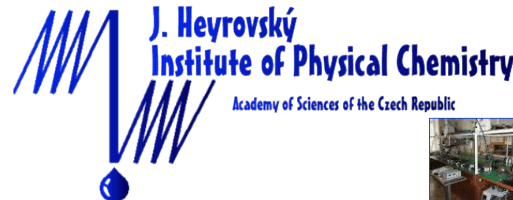
Elektronová struktura molekul

Lubomír Rulíšek, Martin Srnec

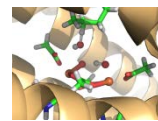
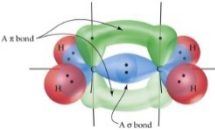
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ÚOCHB AV
ČR
IOCB PRAGUE



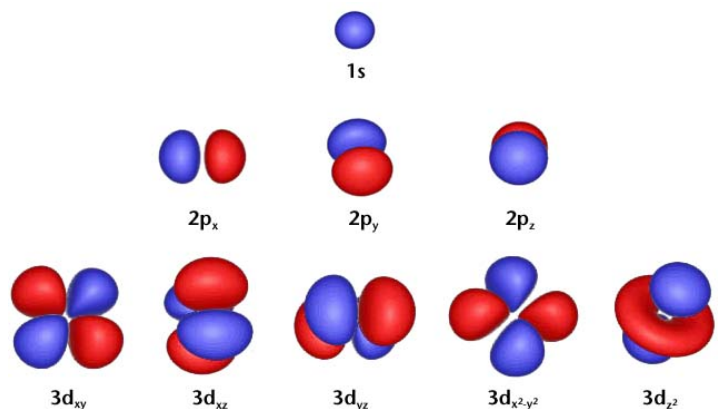
(2016/17: pondělí CH3 8:10–9:40, CH3 9:50–10:35)



Přednáška 6: Od vodíku k proteinům

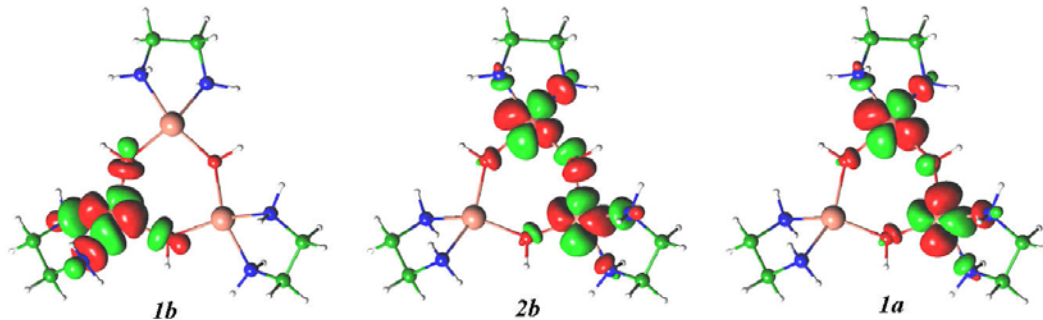
Atomové orbitály vodíku

(„přesné“ jednoelektronové vlnové funkce elektronu v kulově symetrické poli jádra)



Molekulové orbitály „reálných“ systémů

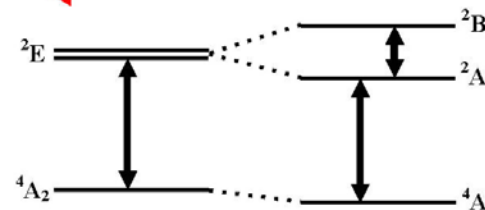
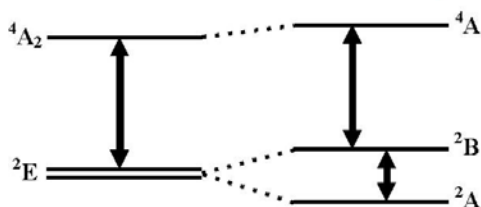
(„přibližné“ jednoelektronové vlnové funkce, jejichž antisymetrizovaný součin nám dá „přibližnou“ vlnovou funkci systému, tedy úplný popis jeho elektronové struktury)

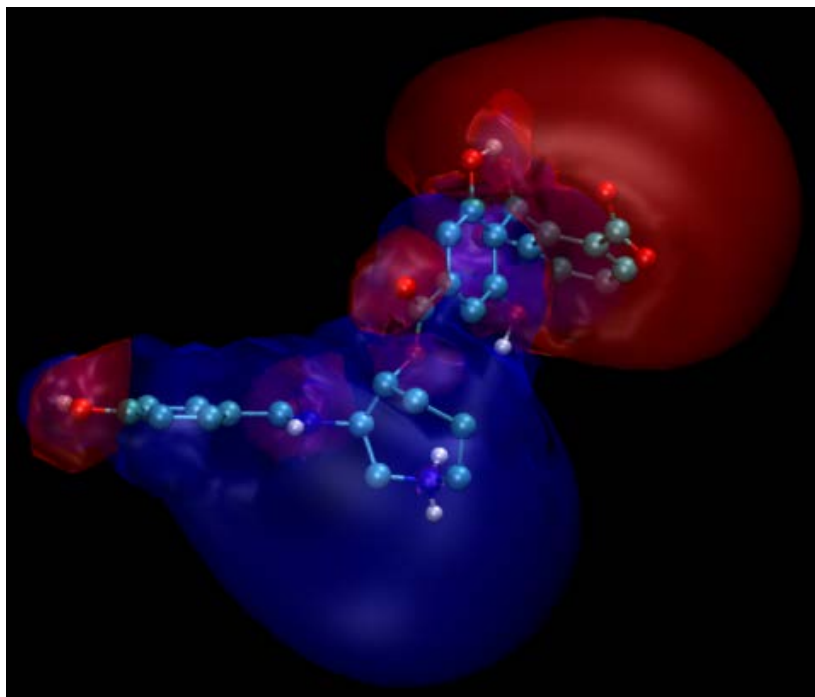
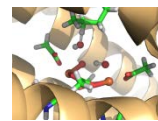
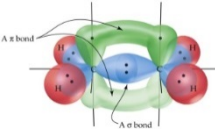


$$1^2A(D_1) \sim 0.61((1a)^\alpha(1b)^2 - (1a)^\alpha(2b)^2) + 0.43(1a)^\alpha(1b)^\beta(2b)^\alpha - 0.25(1a)^\alpha(1b)^\alpha(2b)^\beta$$

$$1^2B(D_2) \sim 0.68((1a)^2(1b)^\alpha + (1b)^\beta(2b)^2) + 0.20((1b)^2(2b)^\alpha - (1a)^2(2b)^\alpha)$$

$$1^4A(Q_1) \sim 1.00(1a)^\alpha(1b)^\alpha(2b)^\beta$$



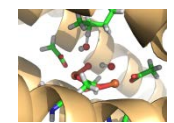
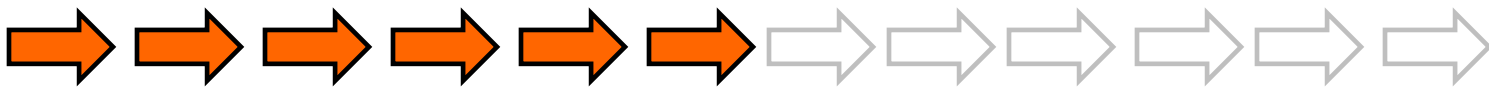
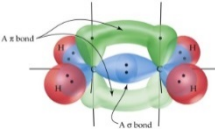


Schrödinger Equation

$$\hat{H}|\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle$$

Free-Particle Dirac Equation

$$H = T = \begin{pmatrix} mc^2 & c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}} \\ c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}} & -mc^2 \end{pmatrix}$$



Q-Chem World

Wave Function Theory

$$\hat{H}_e \Psi_e(\mathbf{r};\mathbf{R}) = E_e \Psi_e(\mathbf{r};\mathbf{R})$$

Variational, perturbational treatment, (QMC)

- HF
- MR-SCF (CASSCF)
- CI
- MP2
- CASPT2
- CCSD(T)
- MR-CI
- FCI

Hierarchy



Density Functional Theory (DFT)

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho]$$

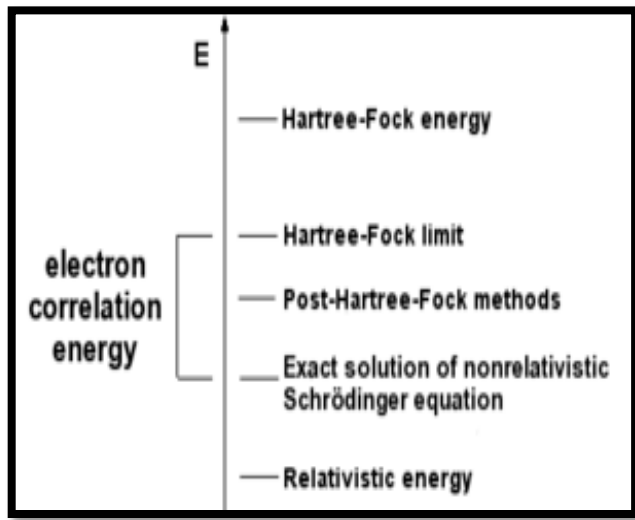
$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

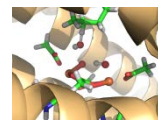
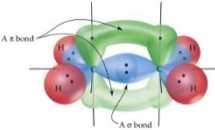
Hundreds of functionals available

- Local density approximation (LDA)
- Generalized gradient approx. (GGA)
- Meta-GGA
- Hybrid (+HF exchange)
- + (empirical dispersion, density-fitting)

John Perdew: Jaccob's Ladder?

“LR personal pick”:
PBE, TPSS(h), B3LYP,
M06's, wB97XD





Víceelektronové atomy, lineární molekuly, nelineární molekuly

Bornova-Oppenheimerova aproximace

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}},$$

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}.$$

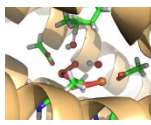
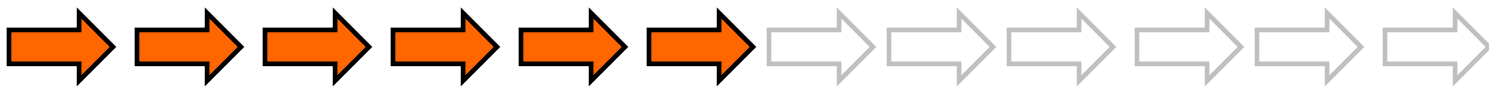
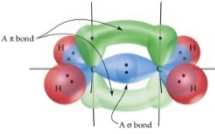
$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}).$$

\mathbf{V}_{eN} nám neumožňuje provést separaci, proměnných, $\Psi(\mathbf{r}, \mathbf{R}) = \Psi(\mathbf{r})\chi(\mathbf{R})$
 my ji přesto provedeme (**BO aproximace**)

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi(\mathbf{r}; \mathbf{R})\chi(\mathbf{R})$$

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

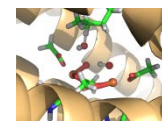
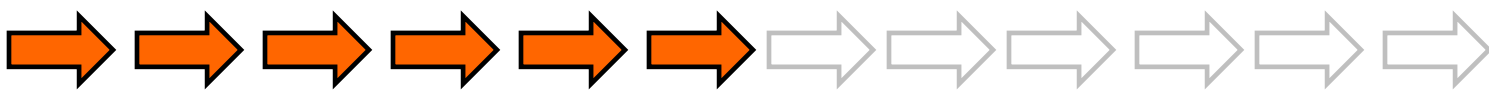
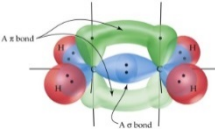
$$\hat{H}_e \Psi(\mathbf{r}; \mathbf{R}) = E_e \Psi_e(\mathbf{r}; \mathbf{R})$$



Tvar vlnové funkce (vícečásticové systémy)

Přednáška číslo 1: **Pauliho vylučovací princip**

- $|\Psi\rangle = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$
- Částice (elektrony, protony) jsou identické – rys kvantové mechaniky
- Pro fermiony (elektrony)
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n) = -\Psi(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \dots, \mathbf{r}_n)$$
- Pro bosony (fotony, atomová jádra)
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n) = \Psi(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \dots, \mathbf{r}_n)$$
- Pauliho vylučovací princip: žádné fermiony nemohou být ve stejném stavu
- Nemůžeme říci, že jeden elektron je zde, a druhý tam, jde vždy o pár elektronů...



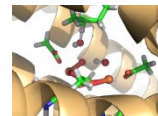
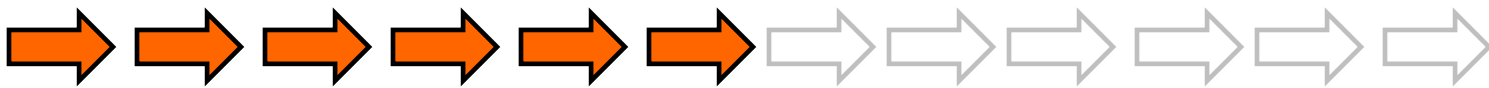
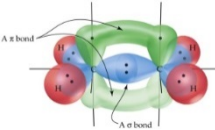
Hartreeho součin (bosony)

$$\mathbf{X}(r_1, r_2, r_3, \dots, r_n) = \chi_1(r_1) \chi_2(r_2) \dots \chi_n(r_n)$$

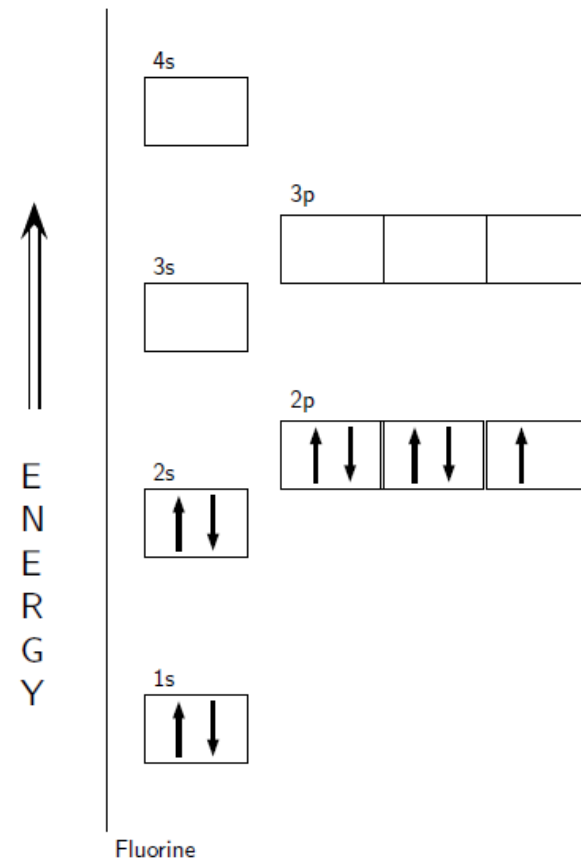
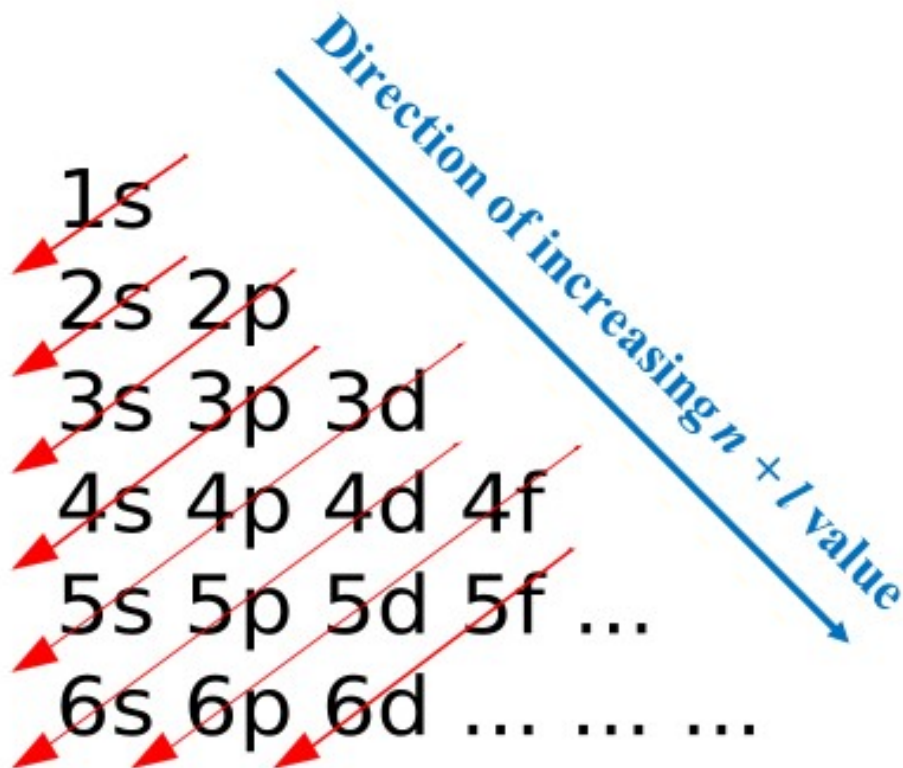
Antisymetrizovaný Hartreeho součin: **Slaterův determinant** (fermiony)

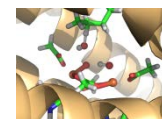
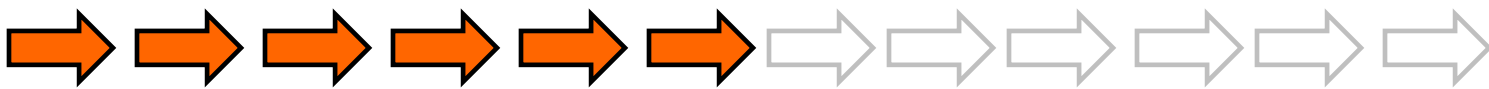
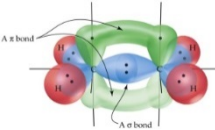
$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix}$$

Atomový či molekulový orbital



Výstavbový princip (Aufbau principle)





N-elektronové stavy v atomech

El. konfigurace: počet elektronů v daných atomových (molekulových) orbitalech

Příklad: **Ni** = [Ar]4s²3d⁸, [Ar]4s¹3d⁹, [Ar]4s⁰3d¹⁰

Cu = [Ar]4s¹3d¹⁰, [Ar]4s¹3d¹⁰

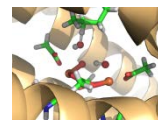
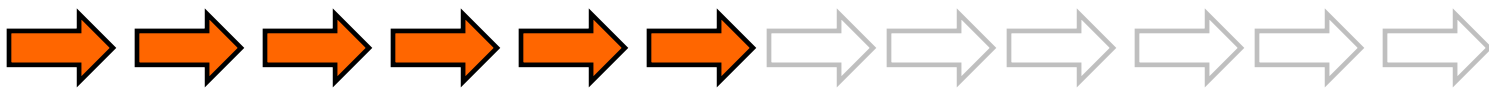
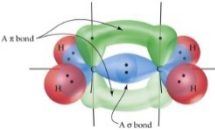
dobře popsány pomocí momentu hybnosti

$$2S+1 L_J$$

Podrobná kuchařka, jak pro danou konfiguraci vyrobit všechny termy:

https://en.wikipedia.org/wiki/Term_symbol (Youtube: Term symbols)

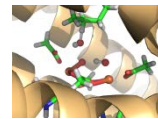
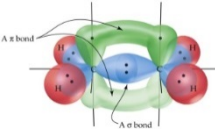
Tabulky



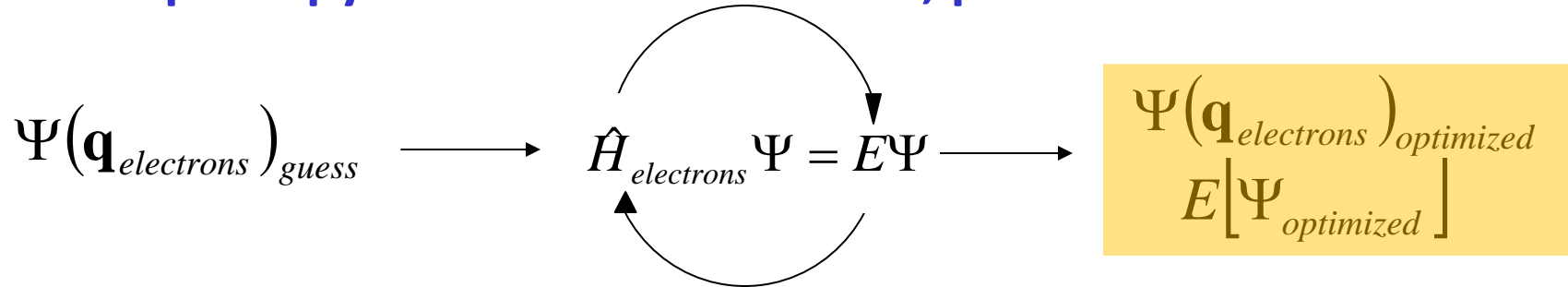
Hundova pravidla

základní elektronový stav molekuly vždy, excitované stavy většinou

1. Pro danou elektronovou konfiguraci má nejnižší energii člen s nejvyšší multiplicitou, tedy i s maximální velikostí celkového spinu.
2. Při dané multiplicitě má nejnižší energii konfigurace s maximální velikostí orbitálního momentu hybnosti, tedy s maximální hodnotou orbitálního kvantového čísla.
3. Má-li atom valenční slupku zaplněnou méně jak z půlky, nabývá v základním stavu hodnota celkového momentu hybnosti $\mathbf{J} = \mathbf{L} + \mathbf{S}$ minimální hodnoty. Je-li valenční slupka zaplněna více jak z půlky, nabývá hodnoty maximální.



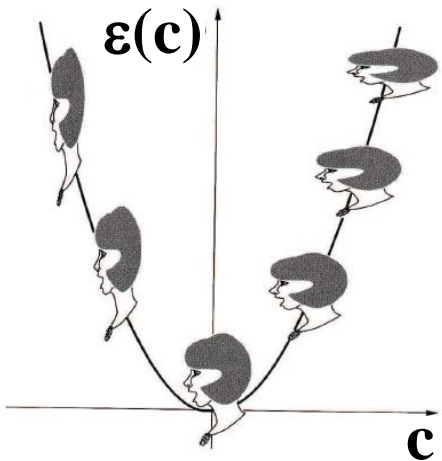
Obecné přístupy k řešení SchR: variační, perturbační



Optimize Ψ and obtain E through a **variation**

$$\varepsilon[\Psi_{guess}] = \frac{\langle \Psi_{guess} | \hat{H}_{electrons} | \Psi_{guess} \rangle}{\langle \Psi_{guess} | \Psi_{guess} \rangle} \geq E[\Psi_{opt}] = \frac{\langle \Psi_{opt} | \hat{H}_{electrons} | \Psi_{opt} \rangle}{\langle \Psi_{opt} | \Psi_{opt} \rangle}$$

$$\varepsilon[\Psi(c_0, c_1, \dots, c_p)] \quad \frac{\partial \varepsilon(c_0, c_1, \dots, c_p)}{\partial c_i} = 0$$



Optimize Ψ and obtain E through a **perturbation**

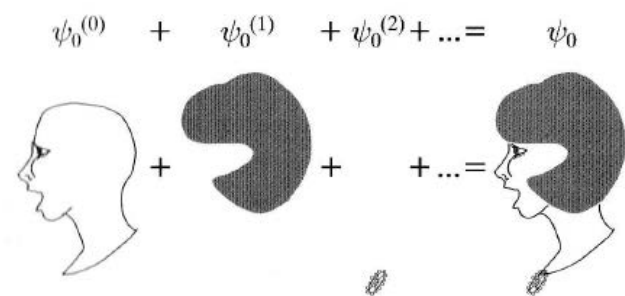
$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{V} \quad \text{Let } \lambda \text{ be a perturbational parameter} \quad 0 \leq \lambda \leq 1$$

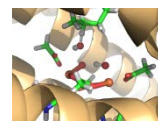
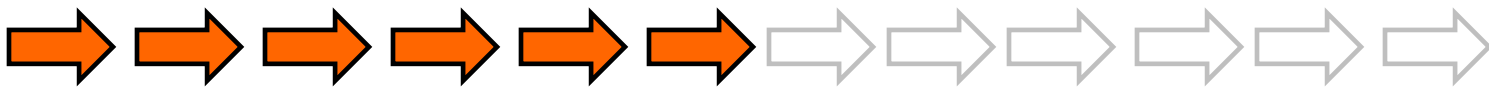
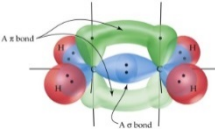
We seek the solution in the form:

$$\Psi(\lambda) = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

Then, solving $\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$





Kvantová chemie: WFT (níže), DFT(dále)

Aneb jak vyřešit SchR pro atomové a molekulové systémy

Semi-empirické metody (MNDO, AM1, PM3, etc.)

Ab initio metody

Hartree-Fock
(HF-SCF)

Multiconfigurational HF
(MCSCF, CASSCF)

perturbational hierarchy
(MP2, MP3, MP4, ...)

perturbational hierarchy
(CASPT2, CASPT3)

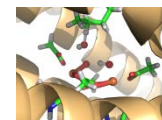
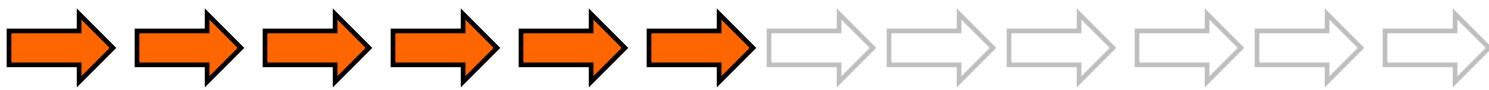
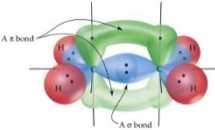
Korelační energie
(většinou <1% celkové energie)

excitation hierarchy
(MR-CISD, MR-CCSD)

excitation hierarchy
(CIS, CISD, CISDT, ...)
(CCS, CCSD, CCSDT, ...)

Full CI

Výpočetní náročnost

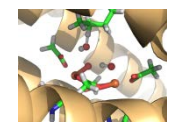
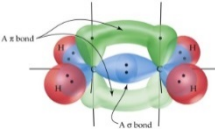


Nástin Hartreeho-Fockovy(-Roothanovy) metody alias SCF metody

Antisymetrizovaný Hartreeho součin: **Slaterův determinant**

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix}$$

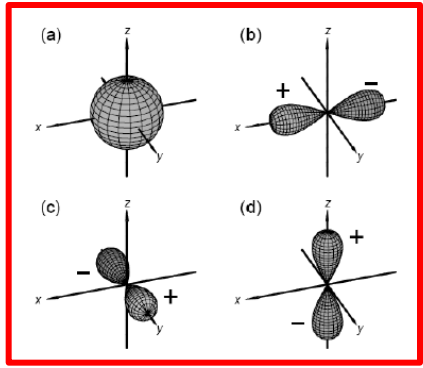
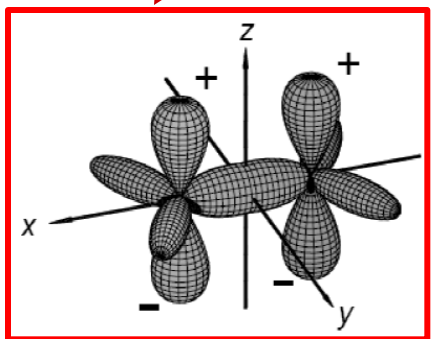
Atomový či molekulový orbital



Molekulové orbitály, coby prvky Slaterova det., jsou konstruovány z atomových orbitalů:

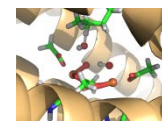
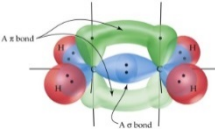
Sada bázových funkcí (basis set)

$$\psi_i = \sum_{j=1}^N C_{ai} \varphi_a \quad (\text{lineární kombinace atomových orbitalů, LCAO})$$



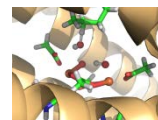
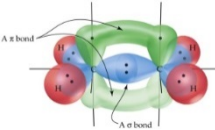
Hydrogen-like (one-electron) AOs are always of the form:

$\varphi(r, \theta, \varphi) = R(r)Y_{lm}(\theta, \varphi)$ where $R(r)$ is the radial component that decays exponentially with increasing distance from the nucleus $e^{-\zeta r}$



Báze atomových orbitalů

DZ
DZP
TZ
TZP
TZPD
QZVPD

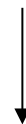


HF rovnice: Co se stane, když dosadíme SD to Schr. rovnice?

$$\hat{H}_{electrons} \Psi(r_{electrons}) = E \Psi(r_{electrons})$$



$$\frac{\langle \Psi | \hat{H}_{electrons} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E$$



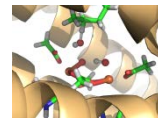
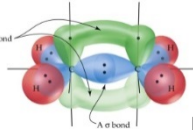
if $\langle \Psi | \Psi \rangle = 1$

$$\sum_i \langle \Psi | \hat{h}_{one-electron,i} | \Psi \rangle + \sum_{i < j} \langle \Psi | \hat{h}_{two-electron,ij} | \Psi \rangle = E$$

Slaterova-Condonova pravidla

(působení jedno a dvou-elektronových operátorů na SD)

$$E = \sum_i \underbrace{\langle \chi_i | \hat{h}_{one-electron} | \chi_i \rangle}_{\text{one-electron integrals}} + \frac{1}{2} \sum_{i,j} \left\{ \underbrace{\langle \chi_i \chi_j | \hat{h}_{two-electron} | \chi_i \chi_j \rangle}_{\text{two-electron Coulomb integrals}} - \underbrace{\langle \chi_i \chi_j | \hat{h}_{two-electron} | \chi_j \chi_i \rangle}_{\text{two-electron exchange integrals}} \right\}$$



$$E[\Psi] = \sum_i \langle \Psi | \hat{h}_{one-electron,i} | \Psi \rangle + \sum_{i < j} \langle \Psi | \hat{h}_{two-electron,ij} | \Psi \rangle$$

if Ψ – 1 Slater determinant

spinorbitals

$$E = \sum_i \underbrace{\langle \chi_i | \hat{h}_{one-electron} | \chi_i \rangle}_{\text{one-electron integrals}} + \frac{1}{2} \sum_{i,j} \left\{ \underbrace{\langle \chi_i \chi_j | \hat{h}_{two-electron} | \chi_i \chi_j \rangle}_{\text{two-electron Coulomb integrals}} - \underbrace{\langle \chi_i \chi_j | \hat{h}_{two-electron} | \chi_j \chi_i \rangle}_{\text{two-electron exchange integrals}} \right\}$$

Condition: $\langle \chi_i | \chi_j \rangle = \delta_{ij}$

Fock equation $\rightarrow \hat{F} \chi_i = \epsilon_i \chi_i$

MOs \rightarrow LCAO
(and E minimized through variational approach)

$$= \frac{1}{2} \sum_i \langle \psi_i | \hat{J} - \hat{K} | \psi_i \rangle$$

$$\hat{F} = \hat{h}_{one-electron} + \hat{J} - \hat{K}$$

Fock operator = Fockian

orbital energy of j-th MO

Fock matrix in the basis of AOs

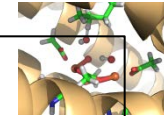
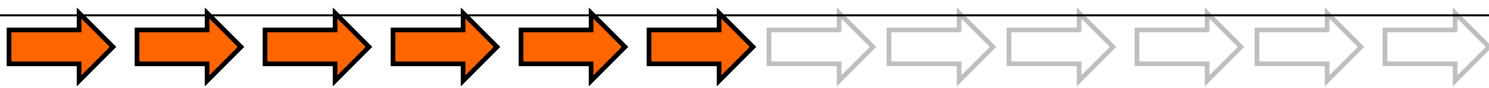
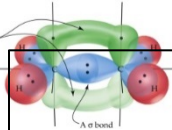
AO-overlap matrix

Vector of LCAO coefficients for j-th MO

Working Roothaan equation: $\{\mathbf{F}(\mathbf{c}) - \epsilon_i \mathbf{S}\} \mathbf{c}_i = 0 \rightarrow \{\mathbf{F}'(\mathbf{c}) - \epsilon_i \mathbf{1}\} \mathbf{c}'_i = 0$

In fact, \mathbf{F} depends on \mathbf{c} : see next page

thus, equations has to be solved iteratively \rightarrow self-consistent field



$$F_{pq} = \left[\langle \varphi_p | \hat{T}_{el} | \varphi_q \rangle - \sum_k^{nuclei} \langle \varphi_p | \hat{V}_{e-n,k} | \varphi_q \rangle \right] + \sum_{r,s} P_{rs} \left[\langle \varphi_p \varphi_r | \hat{V}_{e-e} | \varphi_q \varphi_s \rangle - \frac{1}{2} \langle \varphi_p \varphi_r | \hat{V}_{e-e} | \varphi_s \varphi_q \rangle \right]$$

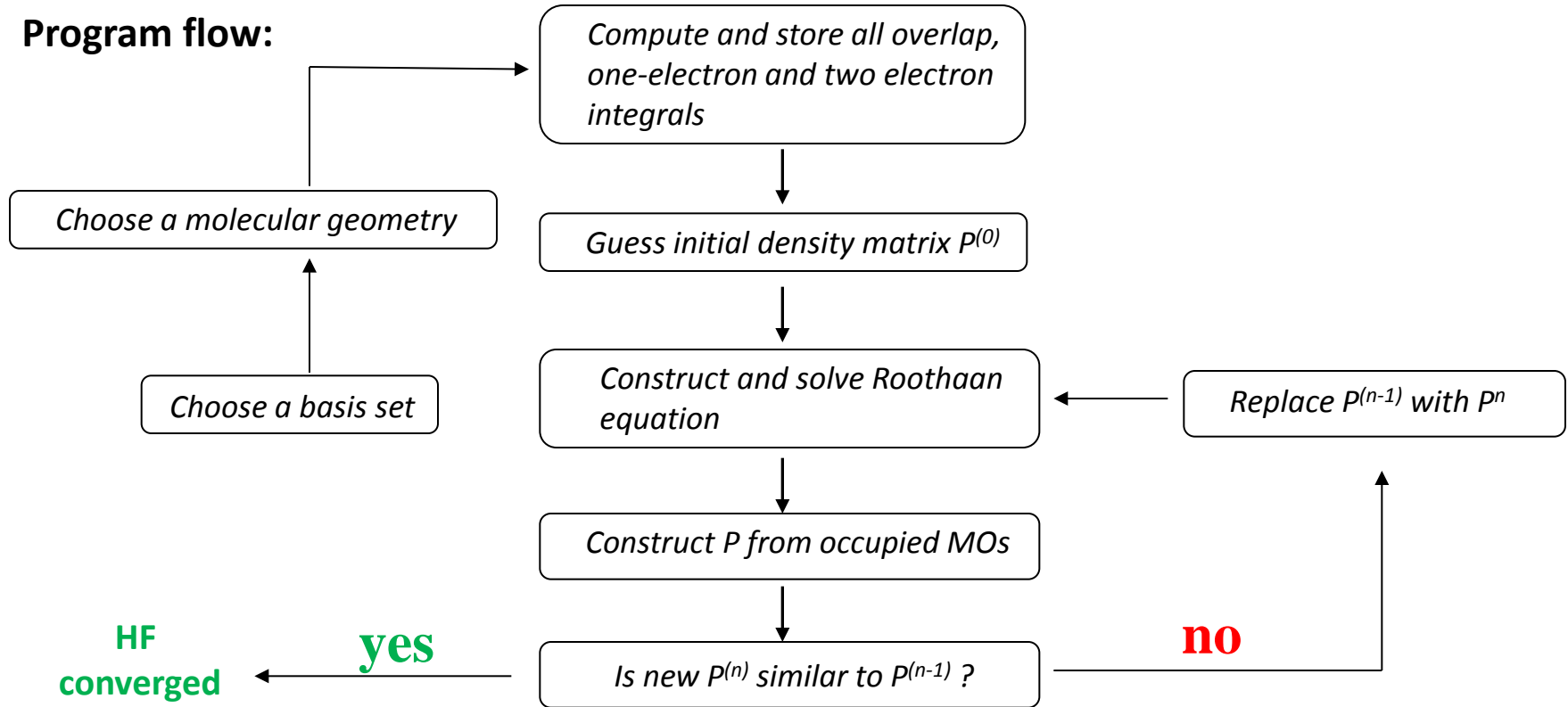
AOs

h_{pq}

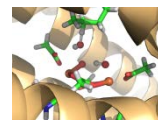
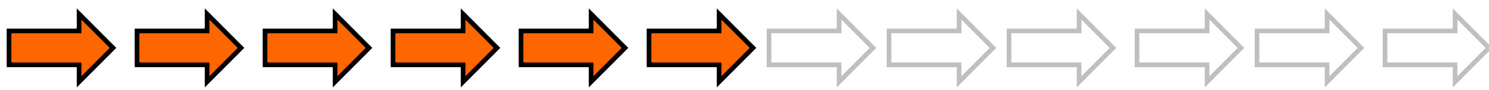
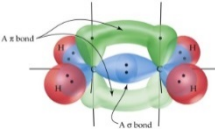
density matrix = $2 \sum_i^{occupied} c_{ri} c_{si}$

This is what is optimized iteratively to get E minimized

Program flow:



$$E_{HF} = \frac{1}{2} \sum_{pq}^{AO} P_{qp} (h_{pq} + F_{pq}) \text{ for restricted Hartree-Fock method}$$



- **Computational bottleneck**
 - the evaluation of two-electron (four-center) integrals

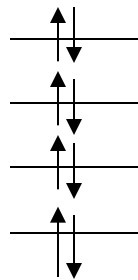
$$\langle \varphi_p \varphi_r | \hat{V}_{e-e} | \varphi_q \varphi_s \rangle$$

- **Restricted (closed-shell / open-shell HF)**
unrestricted HF – spin-symmetry broken

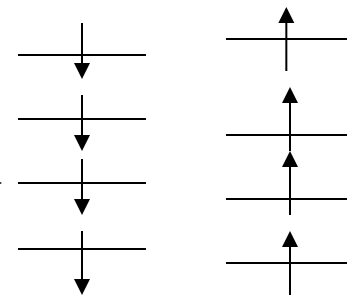
$$\{\mathbf{F}^\alpha - \varepsilon_i^\alpha \mathbf{S}^\alpha\} \mathbf{c}_i^\alpha = 0$$

$$\{\mathbf{F}^\beta - \varepsilon_i^\beta \mathbf{S}^\beta\} \mathbf{c}_i^\beta = 0$$

$$\mathbf{F}^\beta(\mathbf{c}^\beta, \mathbf{c}^\alpha); \mathbf{F}^\alpha(\mathbf{c}^\alpha, \mathbf{c}^\beta)$$



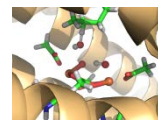
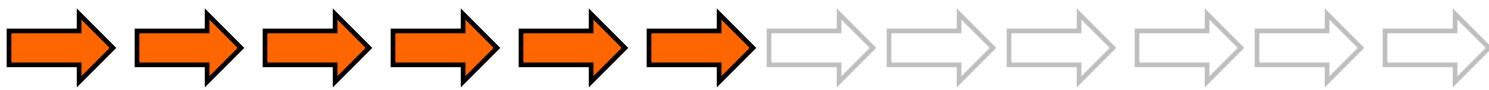
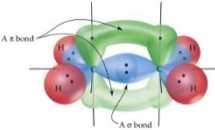
$$S^2 \Psi_{RHF} = \hbar S(S+1) \Psi_{RHF}$$



$$S^2 \Psi_{UHF} \neq \hbar S(S+1) \Psi_{UHF}$$

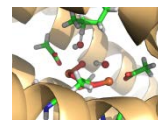
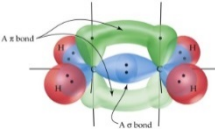
“Spin contamination”

Koopmansův teorém: $IP_i = -\varepsilon_i$



Post-SCF (post-HF) metody

Korelační energie: $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$



DFT metody: 2 základní teorémy

1st Hohenberg-Kohn theorem:

shows that **electron density of an arbitrary molecular system** (in an electronically non-degenerate ground state) in the absence of external electromagnetic fields **determines unambiguously static external potential**

$$v_{ext}(r) = \sum_{k=1}^{nuclei} Z_k |r - R_k|^{-1}$$

2nd Hohenberg-Kohn theorem:

proves that the **correct ground state electron density minimizes the energy $E[\rho]$**

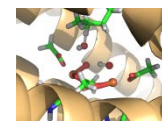
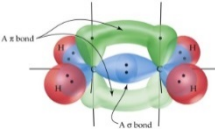
The total energy is represented as a functional of density:

$$E[\rho] = V_{ne}[\rho] + T[\rho] + V_{ee}[\rho] = \int \rho(r) v_{ext}(r) dr + T[\rho] + V_{ee}[\rho]$$

nucleus-electron
attraction energy

kinetic energy
of (interacting) electrons

electron-electron
interaction energy



Molekulové vlastnosti

- Consider a molecule in an external electric field ε .

$$E(\varepsilon) = E(\varepsilon = 0) + \varepsilon \left. \frac{dE}{d\varepsilon} \right|_{\varepsilon=0} + \frac{1}{2} \varepsilon^2 \left. \frac{d^2 E}{d\varepsilon^2} \right|_{\varepsilon=0} + \dots$$

– Dipole moment (μ)

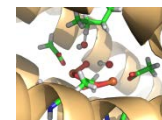
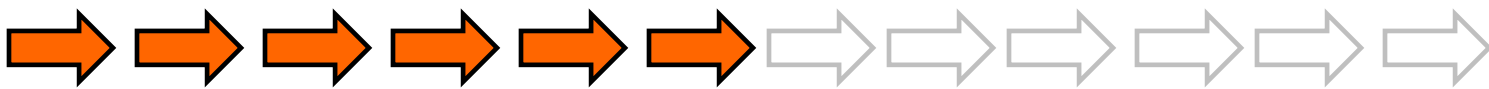
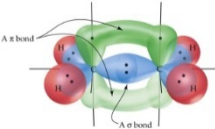
$$\mu = - \left. \frac{dE}{d\varepsilon} \right|_{\varepsilon=0}$$

– Polarizability (α)

$$\alpha = - \left. \frac{d^2 E}{d\varepsilon^2} \right|_{\varepsilon=0}$$

– First hyperpolarizability (β)

$$\beta = - \left. \frac{d^3 E}{d\varepsilon^3} \right|_{\varepsilon=0}$$



Molekulové vlastnosti

$$\frac{dE}{d\varepsilon_\alpha}$$

$$d\varepsilon_\alpha$$

dipole moment; in a similar way also multipole moments, electric field gradients, etc.

$$d^2 E$$

$$d\varepsilon_\alpha d\varepsilon_\beta$$

polarizability

$$d^3 E$$

$$d\varepsilon_\alpha d\varepsilon_\beta d\varepsilon_\gamma$$

(first) hyperpolarizability

$$\frac{dE}{dx_i}$$

$$dx_i$$

forces on nuclei

$$d^2 E$$

$$dx_i dx_j$$

harmonic force constants; harmonic vibrational frequencies

$$d^3 E$$

$$dx_i dx_j dx_k$$

cubic force constants; anharmonic corrections to distances and rotational constants

$$d^4 E$$

$$dx_i dx_j dx_k dx_l$$

quartic force constants; anharmonic corrections to vibrational frequencies

$$d^2 E$$

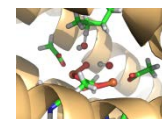
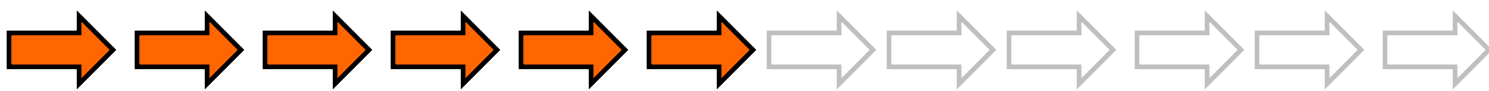
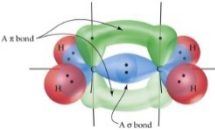
$$dx_i d\varepsilon_\alpha$$

dipole derivatives; infrared intensities

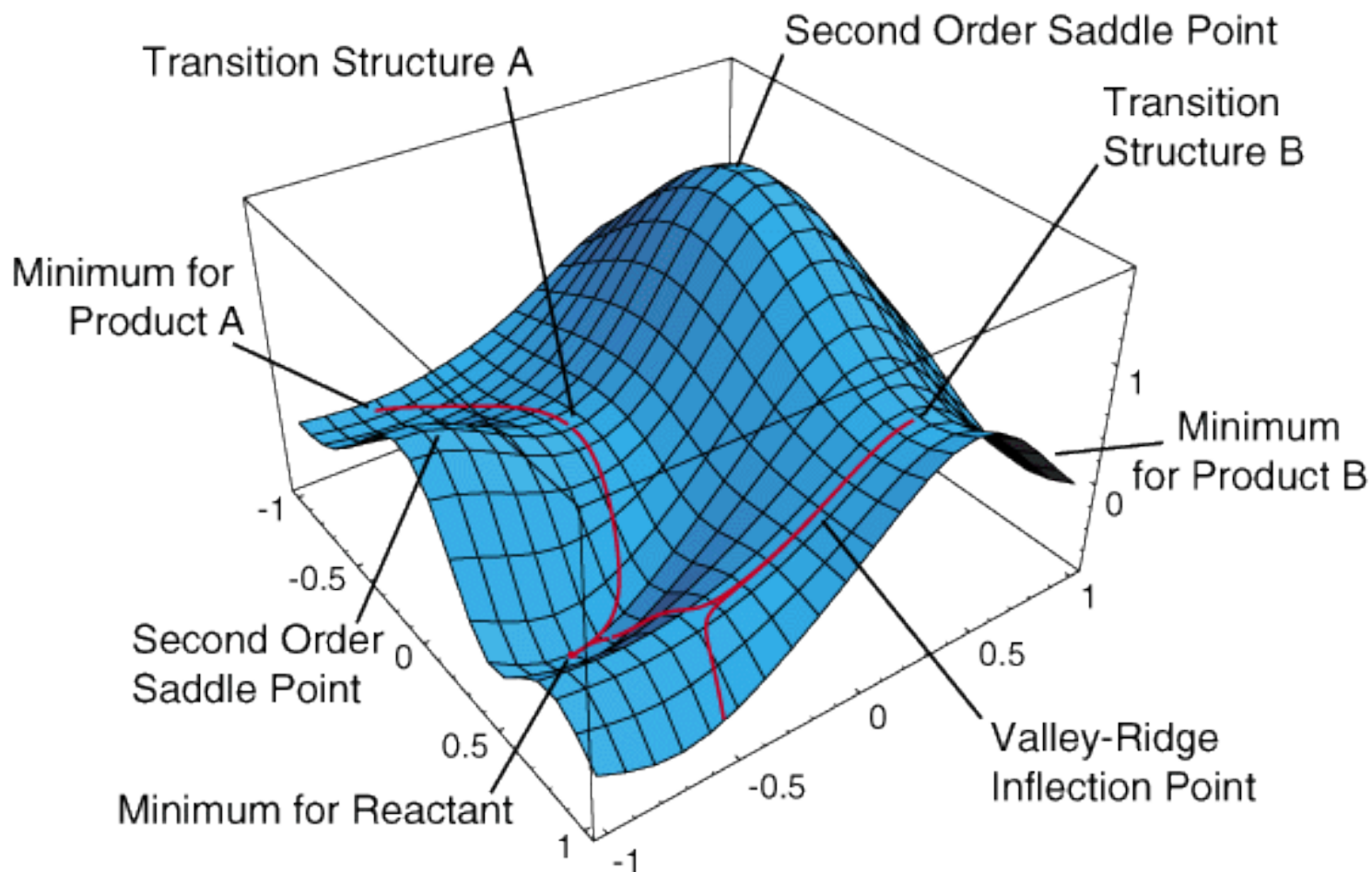
$$d^3 E$$

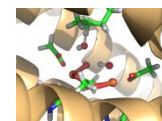
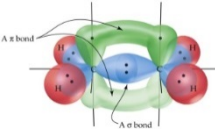
$$dx_i d\varepsilon_\alpha d\varepsilon_\beta$$

polarizability derivatives; Raman intensities



Optimalizace molekulové geometrie





Od vodíku k proteinům

Kvantová chemie: vývoj DFT a WFT metod

Výpočetní chemie: aplikace metod

Molekulové modelování: větší systémy (+Statistická Mechanika, solvatace, molekulová mechanika a dynamika)

Molekulové vlastnosti

Chemická reaktivita: např. teorie aktivovaného komplexu (TST)

Kvantová dynamika

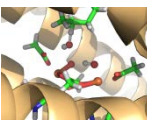
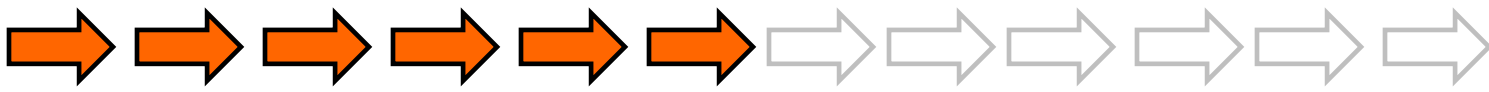
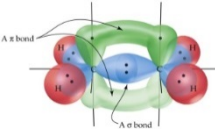
Chemická struktura (př. 1-5): tajemný kvantový svět, formalismus QM, postuláty QM, analytické řešení základních úloh, atom vodíku

Struktura atomů, atomová spektra

Molekulová symetrie

Nevazebné (intermolekulární) interakce

Atomová a molekulová spektroskopie (př. 7-12): obecné principy, MW (rotační), IR (vibrační), Ramanova, CD, EPR, NMR, ...



“God speed, and good luck to you”
(Armageddon)