2. Oktober 2017

1st IWR School

„Mathematical Methods for Quantum Chemistry"

1. Molecular Schrödinger Equation (SE)

$$\hat{H}_{mol}\Psi = E\Psi \qquad \text{time-independent}$$

$$\hat{H}_{mol} = \hat{T}_e + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \left(+ \hat{V}_{ext}\right)$$

$$\hat{T}_e = -\sum_i \frac{1}{2}\vec{\nabla}_i^2 \qquad \vec{\nabla} = \frac{\partial}{\partial x}$$

$$\hat{V}_{ee} = \sum_i \sum_{j \neq i} \frac{1}{|r_i - r_j|}$$

atomic units: $\hbar = 1 = a_0 = e = m_e$

$E = 1$ hartree ≈ 27.211 eV

$627.5 \frac{\text{kcal}}{\text{mol}}$

$$H_{mol}\,\Psi = E\,\Psi$$

Born-Oppenheimer Approximation

$$\Psi = \sum_i \psi_i(R;r)\,\chi(R)$$

$$\hat{H}_{el}\,\psi_e = E_e(R)\,\psi_e$$

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

Quantum Chemistry

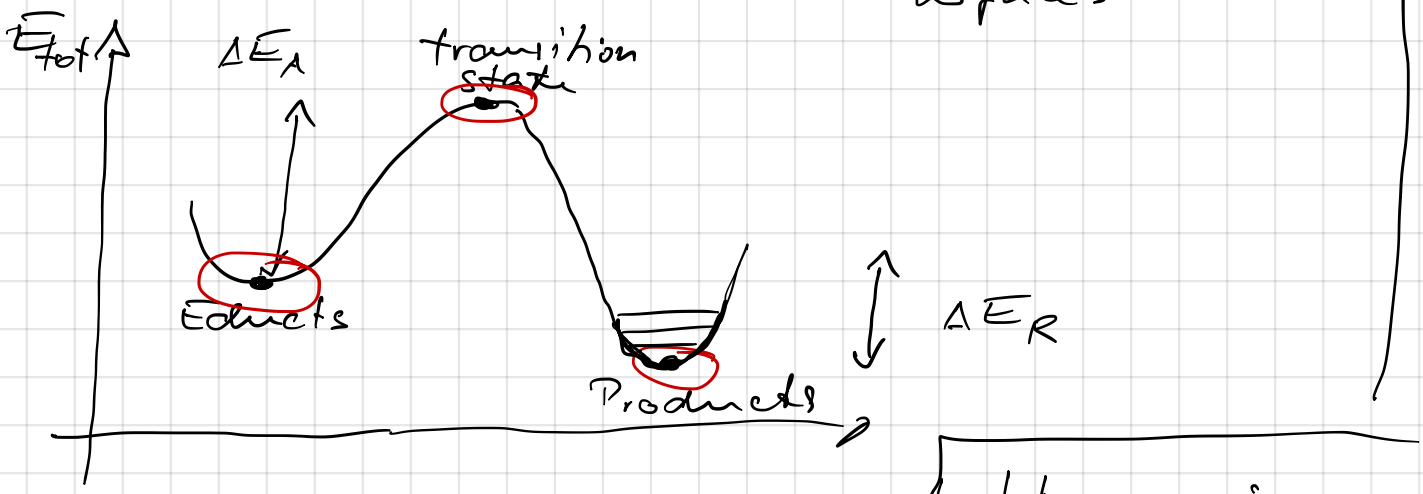
Nuclear Quantum Dynamic

$$\hat{H}_n\,\Theta(R) = E\,\Theta(R)$$

$$\hat{H}_n = \hat{T}_n + \hat{V}_{nn} + E_e(R)$$

$E_{tot}(R)$

Potential Energy Surfaces



Spectroscopic Properties

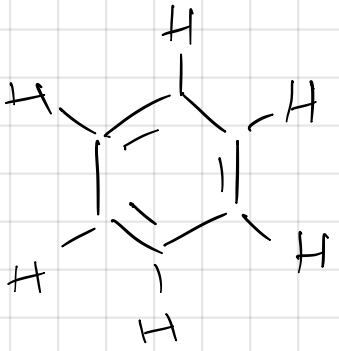
↔ Experiment

Harmonic Oscillator → Vibrations

Rigid Rotator → Rotations

Potential Energy Surfaces

$E_{tot}(\vec{R}_1, \vec{R}_2, \vec{R}_3 \dots \vec{R}_n)$



$\underbrace{10 \cdot 10 \cdot 10 \cdot 10 \cdot \dots \cdot 10}_{10^{30}}$

30 degrees of freedom internal

$\tau = 10^{20}$ s lifetime of the universe

⇒ Analysis to identify the critical points

stationary points $\quad \frac{\partial E_{tot}(R)}{\partial R} \stackrel{!}{=} 0 = \vec{\nabla} E$

characterize $\quad \frac{\partial^2 E}{\partial R_i \partial R_j} = (\underline{H})_{ij}$

⇒ diagonalize

$$diag(\underline{H}) = \begin{pmatrix} k_1 & & 0 \\ & k_2 & \\ & & \ddots \\ 0 & & k_n \end{pmatrix} (\nu_1, \nu_2 \dots \nu_n)$$

k_i: force constants $\quad \nu_i$ = normal modes

all $k > 0$: minimum on PES
„stable isomer"

all $k > 0$ except one!

transition state

all other stationary points are meaningless.

Electronic Schrödinger Equation

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

R: nuclear
r = electronic

$$\hat{H}_e = -\sum_i^n \frac{1}{2}\nabla_i^2 - \sum_i^n \sum_K^m \frac{Z_K}{|r_i - R_K|} + \underbrace{\sum_i^n \sum_{j<i}^n \frac{1}{|r_i - r_j|}}_{\text{two-electron operator}}$$

Hartree-Fock approximation

$$\Psi_e(r_1, r_2 \ldots r_n) = \varphi_1(r_1)\,\varphi_2(r_2)\,\varphi_3(r_3) \ldots \varphi_n(r_n)$$

Electrons are Fermions!

$$\Phi^{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \varphi_1(r_2) & \varphi_1(r_3) & \cdots & \varphi_1(r_n) \\ \varphi_2(r_1) & & & & \\ \vdots & & & & \\ \varphi_n(r_1) & & & & \varphi_n(r_n) \end{vmatrix}$$

Slater-Determinant

$$\Psi(1,2) = \left(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_2(1)\right)\frac{1}{r_2}$$

HF theory $\quad \Psi_e = \Phi_0$

Find the optimal single-particle functions that minimize the energy!

$$E[\Phi_0] = \frac{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \geq E_{exact}$$

Rayleigh-Ritz Variational Principle

convert it $E[\{\varphi_i\}] \rightarrow \dfrac{\delta E[\{\varphi_i\}]}{\delta \varphi_i}$

$$= \frac{\delta E[\{\varphi_i\}]}{\delta \varphi_i^*} \overset{!}{=} 0$$

Slater-Condon Rules

$$\langle \Phi_0 | \hat{O}_1 | \Phi_0 \rangle = \sum_i^n \langle \varphi_i | \hat{O}_1 | \varphi_i \rangle$$

1-particle operator

$$\langle \Phi_0 | \hat{O}_2 | \Phi_0 \rangle = \sum_i \sum_{j<i} \langle \varphi_i^{(1)} \varphi_j^{(2)} | \hat{O}_2 | \varphi_i^{(1)} \varphi_j^{(2)} \rangle - \langle \varphi_i^{(1)} \varphi_j^{(2)} | \hat{O}_2 | \varphi_j^{(1)} \varphi_i^{(2)} \rangle$$

$$\langle ij || ij \rangle = \iint \varphi_i^*(1) \varphi_j^*(2) \frac{1}{|r_1 - r_2|} \varphi_i(1) \varphi_j(2) \, d1 \, d2 - \iint \varphi_i^*(1) \varphi_j^*(2) \frac{1}{|r_1 - r_2|} \varphi_j(1) \varphi_i(2) \, d1 \, d2$$

$$E^{HF}[\{\varphi_i\}] = \sum_i \langle i | \hat{T}_e + \hat{V}_{ne} | i \rangle + \sum_i \sum_{j<i} \langle ij \| ij \rangle$$

$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ add this constraint to the Functional

$$+ \sum_i \sum_{j<i} \lambda_{ij} \left[\delta_{ij} - \langle \varphi_i | \varphi_j \rangle \right]$$

$$\frac{\delta E^{HF}}{\delta \varphi_i} = \frac{\delta E^{HF}}{\delta \varphi_i^*} = \frac{\partial E^{HF}}{\partial \lambda_{ij}} \stackrel{!}{=} 0$$ for the optimal φ_i ?

$$\left(\hat{T}_e + V_{en}\right)|k\rangle + \sum_{i \neq k} \langle i | \frac{1}{r_{12}} | i \rangle | k \rangle$$

$$- \sum_{i \neq k} \langle i | \frac{1}{r_{12}} | k \rangle | i \rangle$$

$$- \sum_i \lambda_{ik} |i\rangle = 0$$

Exchange operator

$$\sum_{i \neq k} \int \frac{\varphi_i^* \varphi_i}{|r_1 - r_2|} \hat{P}_{12} dr_2 \, \varphi_k$$

$$\left[\hat{T}_e + \hat{V}_{en} + \sum_{i \neq k} \int \frac{\varphi_i^* \varphi_i}{|r_1 - r_2|} dr_2\right] \varphi_k = \sum_i \lambda_{ik} \varphi_i$$

Coulomb-Interaction

mean-field

$$\hat{f}\,\varphi_i = \varepsilon_i \cdot \varphi_i$$ Hartree-Fock equation

$\hat{f}$: Fock-Operator

$$: \hat{T}_e + \hat{V}_{en} + \sum_i^n \int \frac{\varphi_i^*(2)\,\varphi_i(2)\,(1-\hat{P}_{12})}{|r_1 - r_2|}\, d\tau_2$$

Self-consistent field – iteratively!

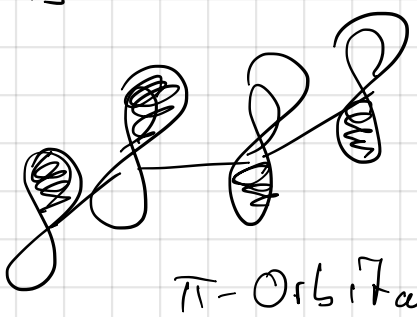
1. Guess first set of single-particle functions
2. Build $\hat{f}$
3. Solve HF equation

$$\varphi_i^{(0)} \overset{2}{=} \varphi_i^{(1)} \qquad \varepsilon_i^{(0)} \overset{2}{=} \varepsilon_i^{(1)}$$

at the end set of converged φ_i, ε_i

Kanonical HF orbitals

Orbital energies



π-Orbitals

90% of the probability to find the electron

$|\varphi_i|^2$

Hartree Fock energy

$$E_0^{HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \neq \langle \Phi_0 | \hat{f} | \Phi_0 \rangle = \sum_i \langle \varphi_i | \hat{f} | \varphi_i \rangle = \sum_i \varepsilon_i$$

$$E_0^{HF} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle$$

Meaning of ε_i

- $-\varepsilon_i$ = Ionization potential i: occupied
- $-\varepsilon_a$ = Electron affinity a: unoccupied

φ_i : remaining Role

How to do this on a Computer?

$$\varphi_i = \sum_{\mu}^{N_{bas}} c_{i\mu} \chi_\mu$$

molecular orbitals — atomic

χ_μ : basis functions → atomic orbitals

Slater-type functions

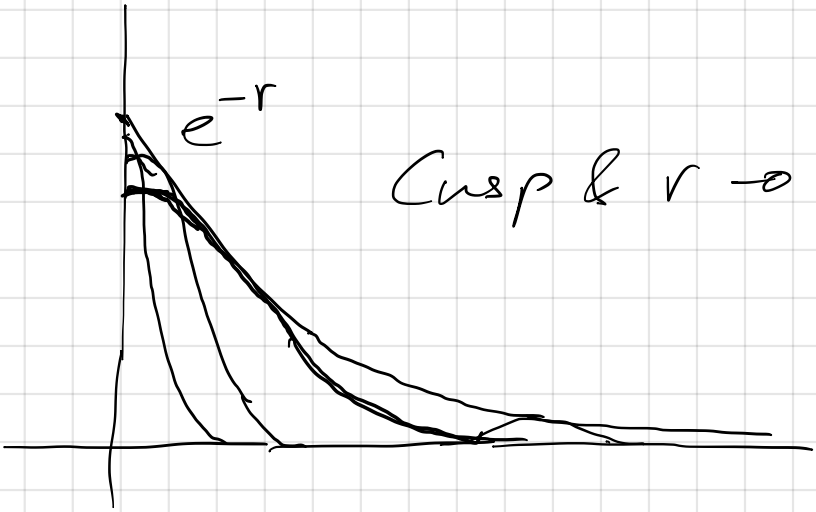
$R \sim e^{-\zeta r}$

Gaussian $R \sim e^{-zr^2}$

atom-centered

$$R_e(r) = (x - X_n)^{l_x} (y - y_n)^{l_y} (z - z_n)^{l_z} e^{-\alpha |\vec{r} - \vec{R}_n|^2}$$

$\langle \mu\nu \,||\, \lambda\sigma \rangle$ four index integrals are easy to solve for Gaussians



Cusp & $r \to \infty$ problems

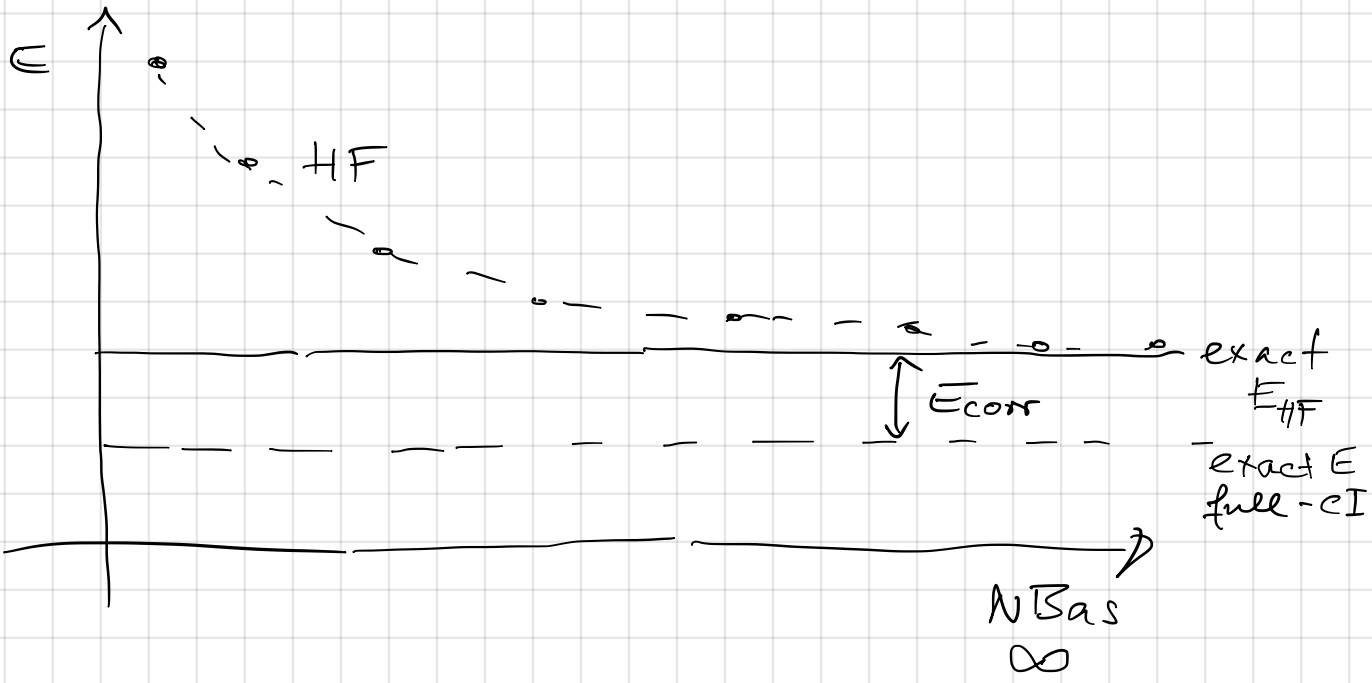
What's missing in HF?

→ Electron correlation!

in HF 95% total energy

missing 5% decisive –

total energy: energy release when you bring n electrons and n nuclei from infinity together



Chemical accuracy:

1 kcal/mol in rel. energies

0.001 Å in bond lengths