

Polyatomic bonding -09 -mod, Notes (13) – Engel 16-17



Balance:

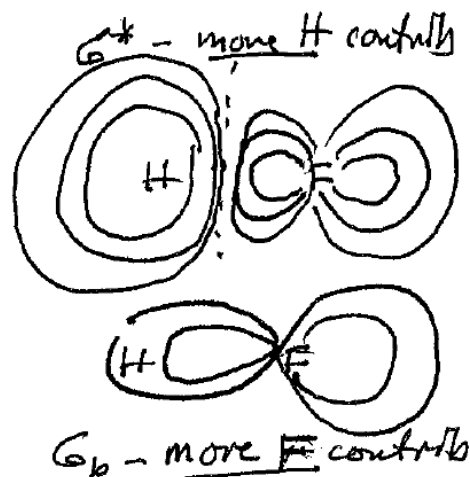
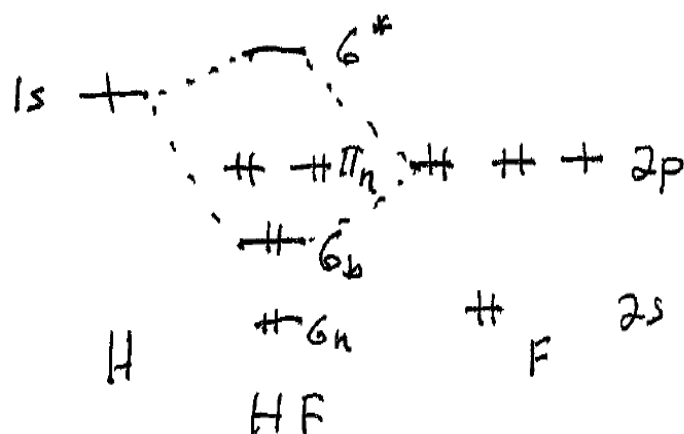
→ nuclear repulsion, positive → ∞

→ e-n attraction, neg. → united atom AO ϵ_i
applies to all bonding, just more nucleirepulsion biggest at low separation, attraction at high - **minimum**

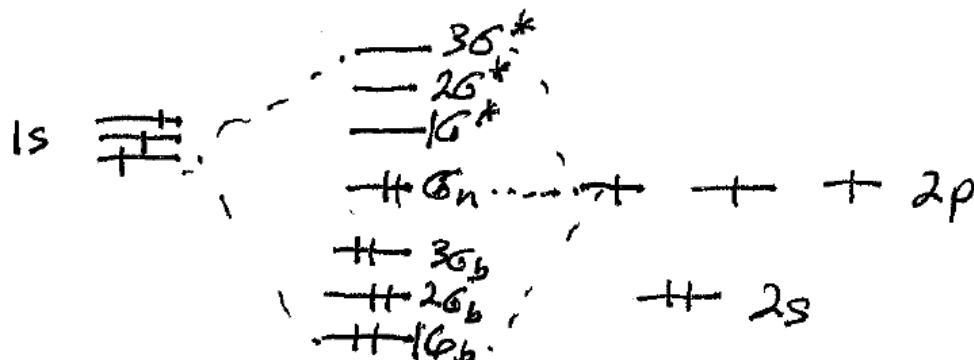
Extend LCAO-MO for Simple Polyatomics,

1st - Hetero atom diatomic bonding - Engel Ch.16.11,
requires adjustment to homonuclear diatomic pictureConsider H-F - F more electronegative, *higher IP* than H

If ionize, electron goes to vacuum, free to fly away

Free - both same, **bigger IP means more negative energy***Ex. HF bonding*Result: bonding MO is closer in energy to F 2p than H 1s,
 σ_b will look more like F-2p, and with 2 electrons, it will
have more electron density close to F than to H→ create a dipole moment by displace e^-

Same idea for polyatomics, keep track of identical atom
e.g. NH_3 – consider only valence electrons F(2s,2p) H(1s)



split of bonding from non bond is large, bonds are strong

Note – all σ , no π - separation of p_x , p_y not preserved,

easiest way for chemist – hybrid idea

- bonding interaction bigger energy than s-p split
- “promote” s equivalent to p
- treat s, p as virtually degenerate—can mix

$sp^3 \rightarrow$ 4 orbitals point at apex tetrahedral

$sp^2 \rightarrow$ 3 orbitals – 120° apart (leaves $p_z \rightarrow \pi$) double bond

$sp \rightarrow$ 2 orbitals – 180° apart ($p_{x,y}$ orbital $\rightarrow 2\pi$) triple bond

$$sp^3_1 = s + p_z + p_x + p_y$$

$$sp^3_2 = s + p_z - p_x - p_y$$

$$sp^3_3 = s - p_z + p_x - p_y$$

$$sp^3_4 = s - p_z - p_x + p_y$$

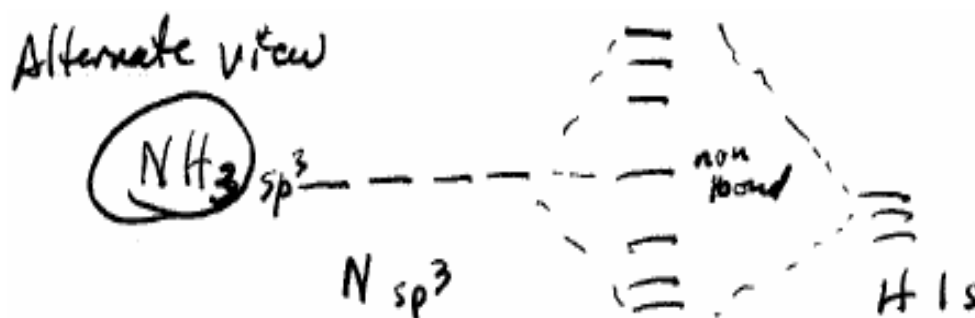
$$sp^2_1 = s + p_x + p_y$$

$$sp^2_2 = 2s - p_x - p_y$$

$$sp^2_3 = p_x - p_y$$

$$sp_1 = s + p_z$$

$$sp_1 = s - p_z$$



All of these take some chemical intuition
 balance electronegativity and how molecules form
 C_2H_2 –linear, C_2H_4 –planar, { NH_3 non planar, BH_3 planar}

A little more depth

We took simplistic separation approach

How do we **evaluate energies / realistic wave/fct**

imagine AO's as a basis set of orbitals – “guesses”

$$\langle H \rangle = \int \phi_i H \phi_i / \int \phi_i \phi_i = H_{ii} / S_{ii} \quad \text{expectation value } (i,i)\text{-diagonal}$$

$$\langle H \rangle = \int \phi_i H \phi_j / \int \phi_i \phi_j = H_{ij} / S_{ij} \quad \text{interaction value } (i,j)\text{-off-diagonal}$$

These are called **Coulomb integrals** (H_{ij}) – energy operator
 which are normalized to **overlap integrals** (S_{ij})

So if $\psi = \sum c_i \phi_i$ i.e. if MO made of AOs, then want to
optimize c_i -- use **variation principle**: $\partial \langle H \rangle / \partial c_i = 0$

e.g. let: $\psi = c_A \phi_A + c_B \phi_B$ (as in σ_b) then -- **demonstrate**

$$E = [c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}] / [c_A^2 + 2c_A c_B S_{AB} + c_B^2]$$

set $\partial E / \partial c_A = 0$, $\partial E / \partial c_B = 0 \Rightarrow$ 2 equations, 2 unknowns

easiest (Levine) differentiate both sides \rightarrow **secular equations**,

$$\partial \{E [c_A^2 + 2c_A c_B S_{AB} + c_B^2]\} / \partial c_A = \partial \{c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}\} / \partial c_A$$

$$\partial E / \partial c_A [c_A^2 + 2c_A c_B S_{AB} + c_B^2] + E [2c_A + 2c_B S_{AB}] = [2c_A H_{AA} + 2c_B H_{AB}]$$

First term = 0 (min), rest: $0 = c_A (H_{AA} - E) + c_B (H_{AB} - E S_{AB})$ same for H_{BB}

Solution: energies from secular determinant:

(polynomial, quadratic
2 solution – E_1, E_2)

$$0 = \begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix}$$

general wave function (LCAO-MO):

$$\psi = \sum c_i \phi_i$$

“Secular Determinant” n -AOs give n -MOs $\rightarrow n - E_K$ values

$$0 = \begin{vmatrix} H_{11} - E & H_{21} - ES_{21} & \dots & \dots & H_{n1} - ES_{n1} \\ H_{12} - ES_{12} & H_{22} - E & & & \vdots \\ H_{13} - ES_{13} & & \ddots & & \vdots \\ \vdots & & & & \vdots \\ H_{1n} - ES_{1n} & \dots & \dots & \dots & H_{nn} - E \end{vmatrix}$$

Then insert E_K 's into secular equations ($n - equations$)

$$\sum_{ij} (H_{ij} - E_K S_{ij}) c_j^k = 0$$

$n - E_K$ makes n separate sol'n

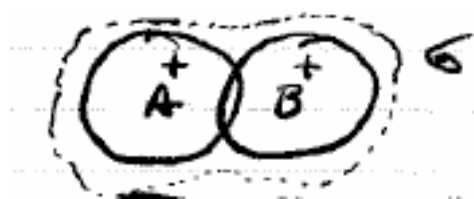
solve set of simultaneous equations for coefficients

\rightarrow get a set of $n - c_i^k$ – for each (n -values) E_K

Delocalization—major aspect of MO model, see above,
all MOs are solutions to *secular determinant* (energies)
and associated set of *secular equations* (wave functions),
 \rightarrow so each has contributions from all the AOs - delocalized

Valence Bond method, *localized* view, chemical appeal

Idea, AOs on one atom overlap those on another
and share and electron pair \rightarrow bond



$$\text{H}_2: \psi_{\text{VB}}(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$$

electrons identical, need both forms,
bonding - increase e^- density between

Contrast this with the MO picture

$$\begin{aligned} \psi_{\text{MO}}(1,2) &= \sigma_b(1) \sigma_b(2) = [\phi_A + \phi_B](1) [\phi_A + \phi_B](2) \\ &= \underbrace{\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)}_{\text{VB } 2 e^- \text{ state}} + \underbrace{\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)}_{\text{ionic states (excited)}} \end{aligned}$$

Difference, MO too much emphasis on ionic states,
VB too much bond strength (e^- all between nuclei)

Bring them together

VB add excited state (ionic) contribution (e^- promoted)

$$\psi_{\text{VB}'}(1,2) = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + \lambda[\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)]$$

MO add excited configuration, $\sigma^*(1) \sigma^*(2)$

$$\begin{aligned} \sigma_b(1) \sigma_b(2) - \lambda'[\sigma^*(1) \sigma^*(2)] = \\ \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) + (1-\lambda')[\phi_A(1)\phi_A(2) + \phi_B(2)\phi_B(1)] \end{aligned}$$

Adjusting λ, λ' will bring these to the same functional form

Can use variation method to optimize λ, λ'

Poly atomic VB \rightarrow select AOs with valence e^- to mix,
share e^- , form $2e^-$ bond, promote e^- to get hybrids
 $\text{C } (2s)^2(2p)^2 \rightarrow \text{C } (2s)^1(2p)^3 \rightarrow \text{C } (sp^3)^4$

Then can form local bonds: C-H: $\phi = \text{C } (sp^3)^1 + \text{H}(1s)^1$

And C-C: $\phi = \text{C}_a(sp^3)^1 + \text{C}_b(sp^3)^1$ etc.

Problem: VB completely **local**, so misses out on delocalized systems like π and interactions between bond networks

VSEPR model — describe molecular geometry

based on **e^- pair repulsion**, in VB – bonds, lone pairs

Minimize energy by distance, spread, open angles

Diatomic – linear, trivial, one bond

Triatomic – linear or bent, depend on lone pairs

O=C=O - two bonds around C, both double, linear

H-O-H - two bonds and two lone pairs around O

Approx tetrahedral, pairs more space

- Rules:**
1. bonds to ligands and lone pairs repel
 2. lone pairs require more angular space than bonds
 3. More electronegative ligand—increase space,
more electroneg. central atom, decrease space
 4. multiple bond needs more space than single bond

Ex. CH₄ –tetrahedral, angle between C-H bonds, 109°

NH₃ – pyramidal, lone pair 4th position, angle ~107°

H₂O – bent, two lone pairs other positions, angle ~105°

CO₂ – linear, SO₂ – bent (lone pair)

C₂H₂ – linear, C₂H₄ – planar, C₂H₆ – each ~ tetrahedral

Solving MO problem for real systems:

Clearly all of this gets complex for large molecules – most quantum chemistry problems solved using computers

$$\psi \sim \sum_i c_i \phi_i^{\text{AO}} \quad \phi_i^{\text{AO}} \sim \sum_k a_k f_k \quad f_k - \text{functions, e.g. STO} \rightarrow e^{-\alpha r}, \\ \text{Gaussian} \rightarrow e^{-\alpha' r^2}$$

sometimes fix a_k 's by some optimization (e.g. solving atoms)

always optimize c_i by minimize energy

can also vary geometry to optimize energy

⇒ structure determination

Hückel Model of π -systems -- a little different

π -bonds – weaker – so usually highest E bond
(Aufbau—last to fill)

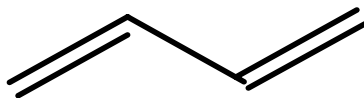
symmetry – out of the plane – not mix with σ -orbital

Hückel Theory – empirical approximation

— solve π -system separately, idea is π not mix with σ

$\psi = \sum_i c_i \phi_i \quad \phi_i = 2p^z_i$ just sum over p^z orbital on atoms i
this ignores the σ orbitals - lower energy

Ex. Butadiene



$$\psi^k = c^k_1 \phi_1 + c^k_2 \phi_2 + c^k_3 \phi_3 + c^k_4 \phi_4$$

normal secular determinant:

$$0 = \begin{vmatrix} H_{11} - \epsilon & H_{12} - \epsilon S_{12} & H_{13} - \epsilon S_{13} & H_{14} - \epsilon S_{14} \\ H_{21} - \epsilon S_{21} & H_{22} - \epsilon & H_{23} - \epsilon S_{23} & H_{24} - \epsilon S_{24} \\ H_{31} - \epsilon S_{31} & H_{32} - \epsilon S_{32} & H_{33} - \epsilon & H_{34} - \epsilon S_{34} \\ H_{41} - \epsilon S_{41} & H_{42} - \epsilon S_{42} & H_{43} - \epsilon S_{43} & H_{44} - \epsilon \end{vmatrix}$$

- Rules:**
1. Let $S_{ij} = 0$ $i \neq j$ -- no overlap between atoms
 2. let $H_{ii} = \alpha$ ($i = j$) -- All treated the same, diagonal
 3. let $H_{ij} = \beta$ $i = j \pm 1$, near neighbor interact
 4. let $H_{ij} = 0$ non-near neighbor do not interact

Hückel secular determinant:

$$0 = \begin{vmatrix} \alpha - \epsilon & \beta & 0 & 0 \\ \beta & \alpha - \epsilon & \beta & 0 \\ 0 & \beta & \alpha - \epsilon & \beta \\ 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix}$$

solution – divide entire

matrix (determinant) by β

then let – $x = (\alpha - \epsilon)/\beta$

$$0 = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

\Rightarrow det - expand by minors (show):

$$x^4 - 3x^2 + 1 = 0$$

solution (just quadratic eq.):

$$x = \pm 0.618, \pm 1.618$$

Plug into: $x = (\alpha - \epsilon)/\beta$ to get expressions for ϵ

$$\epsilon_1^\pm = \alpha \pm 1.618 \beta$$

$$\epsilon_2^\pm = \alpha \pm 0.618 \beta$$

$$\begin{array}{l} 4\pi \text{ ————— } \epsilon_1^- \quad \alpha - 1.618\beta \\ 3\pi \text{ ————— } \epsilon_2^- \quad \alpha - 0.618\beta \\ 2\pi \text{ ————— } \epsilon_2^+ \quad \alpha + 0.618\beta \\ 1\pi \text{ ————— } \epsilon_1^+ \quad \alpha + 1.618\beta \end{array}$$

Butadiene has 4 π -electrons, could have 2 in each orbital:

$\alpha_j \beta$ - neg

$$E_g = 2\epsilon_1^+ + 2\epsilon_2^+$$

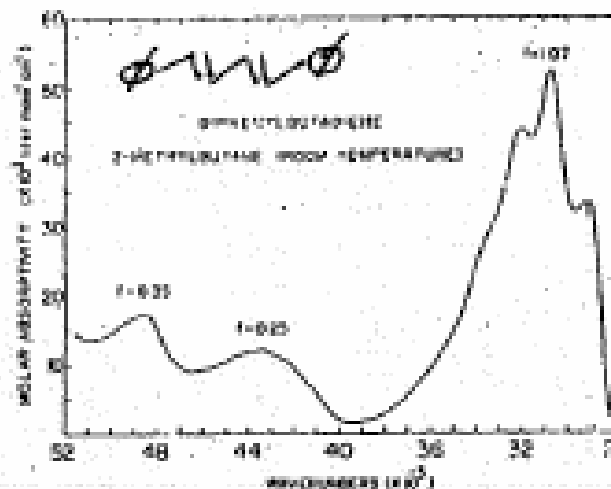
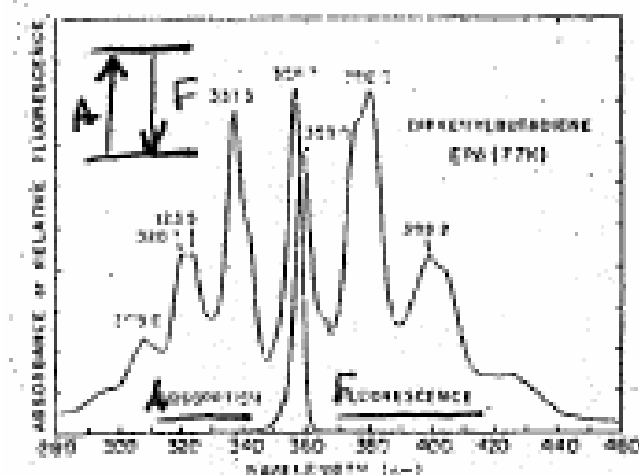
$$= 4\alpha + 4.472 \beta \quad \text{- ground state: } (1\pi)^2 (2\pi)^2$$

$$E_{ex} = 2\epsilon_1^+ + \epsilon_2^+ + \epsilon_2^-$$

$$= 4\alpha + 3.236 \beta \quad \text{- excited state: } (1\pi)^2 (2\pi)^1 (3\pi)^1$$

$$\Delta E = 1.236 \beta$$

– transition in uv:



Plug ε^k into: $\sum_{i=1}^4 (H_{ij} - \varepsilon_k \delta_{ij}) c_j^k = 0$ for $j = 1 - 4$ (δ_{ij} -no S_{ij})

Ex:

$$\begin{aligned} (\alpha - \varepsilon_k) c_1 + \beta c_2 &= 0 \\ \beta c_1 + (\alpha - \varepsilon_k) c_2 + \beta c_3 &= 0 \\ \beta c_2 + (\alpha - \varepsilon_k) c_3 + \beta c_4 &= 0 \\ \beta c_3 + (\alpha - \varepsilon_k) c_4 &= 0 \end{aligned}$$

4 equations (j) solve simultaneously for c_j , repeat each ε^k

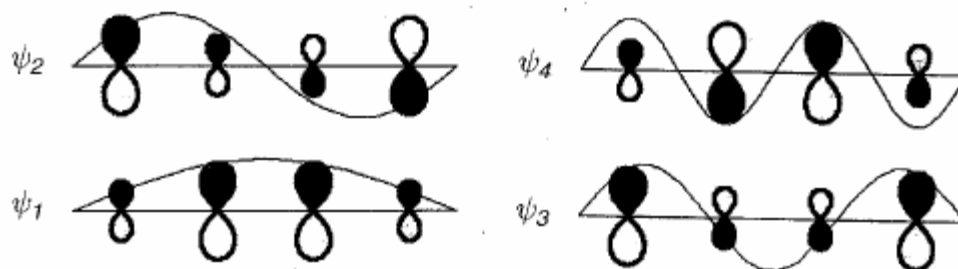
$$\psi_{1\pi} = 0.37 p_1 + 0.60 p_2 + 0.60 p_3 + 0.37 p_4 \quad (0 \text{ nodes})$$

$$\psi_{2\pi} = 0.60 p_1 + 0.37 p_2 - 0.37 p_3 - 0.60 p_4 \quad (1 \text{ node})$$

$$\psi_{3\pi} = 0.60 p_1 - 0.37 p_2 + 0.37 p_3 + 0.60 p_4 \quad (2 \text{ nodes})$$

$$\psi_{4\pi} = 0.37 p_1 - 0.60 p_2 + 0.60 p_3 - 0.37 p_4 \quad (3 \text{ nodes})$$

Hückel MO's (phasing, shapes - side view) for butadiene:



nodes \rightarrow E

Hückel MO's for benzene very similar, but since cyclic get an extra term in determinant, i.e. H_{16} and $H_{61} \neq 0 \rightarrow$ try it!

What if system not π -system?

QM calculational Complexity builds-up

– semi empirical—extend the idea above

Extended Hückel – let atoms differ, calculate S_{ij}

but valence electrons interaction – empirical parameter (i.e. include $\sigma + \pi$ but parameterize H_{ij})

CNDO – MNDO – INDO

– basically variations of neglecting overlap (NDO) and including parameters for H_{ij}

ab initio \rightarrow Compute solution to Schrödinger Equation – no parameters but many approximations –

SCF {typically Hartree-Fock – set up w/f and use to calculate potential ($V(r_i)$) and re-solve -- keep cycling until no change in $V(r_i)$ }

Being a little more precise—add spin:

Multielectron wave function - obey Pauli (anti-symmetric w/r/t exchange of electrons) -- use determinant form:

$$\psi(r_1, r_2, r_3, \dots, r_N) = \begin{vmatrix} \phi_A(r_1) & \phi_B(r_1) & \phi_C(r_1) & \dots & \phi_N \\ \phi_A(r_2) & \phi_B(r_2) & & \dots & \\ \vdots & & & \dots & \\ \phi_A(r_4) & & & & \phi_N(r_n) \end{vmatrix}$$

This will be anti-symmetric w/r/t exchange of electron

i.e. $\psi(r_1, r_2, r_3, \dots) = -\psi(r_1, r_3, r_2, \dots)$ etc.

since exchange electron \rightarrow exchange rows

Still product of one-electron functions (MO) – average $V(r_{ij})$

Solving *ab-initio* problem involves 1-2-3-4 center integrals

Put up example of what it means

big problem with 3 + 4 center \Rightarrow often neglect some
 Gaussian orbitals $g_{nmk}(r) = (x^n + y^m + z^k) e^{-\alpha r^2}$
 make integrals simpler, rep. AOs as: $STO = \sum c_n g_n(r)$

Calculations get very big – tend to scale like $n^4 - n^5$
 n = number basis functions (the $g_n(r)$ above)
 so small molecules very quick (do on PC)
 big molecules become impossible

Methods work well for molecules up to ~ 100 atoms
 (or ~ 1000 basis functions \rightarrow represent AO's)
 multi center integrals \Rightarrow need large memory / disk
 \Rightarrow takes time (now dedicated PC's or **clusters**)

Alternate approach: Density Functional Theory (DFT)

Hohenberg-Kohn \rightarrow $\rho(r)$ electron density for grd state
 in principle can determine w/f: $\psi(r_1, \dots, r_n)$

Advantage – calculations become easier / bigger system

Disadvantage – involves parameters / approximations
 (variation works differently)

[now part of standard Quantum Chemistry programs]

Solution – density \rightarrow orbital \rightarrow density etc. (self-consist)

- Goals: 1. molecular properties → structure, bonding, charge distribution, dipole moments
spectral transitions – IR(vibration) -grd st property
UV (electronic) - more difficult, excited state
2. Structure – optimize geometry – minimum E
3. Kinetics – reaction surface – E as fct geometry

Very large molecules → e.g. proteins / nucleic

Use results of Quantum Mechanics → create $U_{el}(R)$
an energy function that varies with nuclear position

⇒ minimize geometries: molecular mechanic model

⇒ dynamics / trajectories: molecular dynamics