Quantum Methods in Molecular Simulations[†] (CD61006)

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[†]The slides should be used only alongside the lecture instructions, reading materials and derivations worked out during lecture hours. Else, they may not make any sense.





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Η	-1.32697	2.01148	0.00000	0	-0.71475	0.11743	-0.01868
Н	-0.62094	2.01281	0.00000	0	-1.73575	0.48010	0.66657





0	-0.60345	0.43840	0.45675
н	0.36444	0.39261	0.46442
н	-0.88229	-0.47684	0.61017



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R1 = 0.96
R2 = 0.96
A = 104.5



0	-1.12939	-0.68743	-0.06210
0	0.32386	-0.67679	-0.05417
н	-1.24997	0.08909	0.51701
н	0.44444	-1.45330	-0.63328

R1 = 0.97
R2 = 0.97
R3 = 1.45
A1 = 96.6
A2 = 96.6



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н	-1.24997	0.08909	0.51701
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R1 = 0.97
R2 = 0.97
R3 = 1.45
A1 = 96.6
A2 = 96.6
D =







10

Z-matrix

- line 1 C line 2 O 1 R line 3
- line 4 R 0.955

Identify and draw the molecule

line	1	C
line	2	0 1 OC
line	3	H 1 HC 2 A
line	4	H 1 HC 2 A 3 180.0
line	5	
line	6	OC 1.2
line	7	A 120.0
line	8	
line	9	HC 1.08

Write the Z-matrices







OC 1.2



Exercise

	a = b a = f
Cadmium	C.
a = b = 2.979 Å, c = 5.6	5 18 Å
$a = B = 90^{\circ}, x = 120^{\circ}$	

Copper = b = c = 3.615 Å

$$\alpha = \beta = \gamma = 90^{\circ}$$



Reading exercise

Young

Chapter 8: Building molecular geometry

Chapter 9: Constructing Zmatrix

Sholl and Steckel

Chapter 2: DFT calculations for simple solids





$$E_{\rm FF} = E_{\rm str} + E_{\rm bend} + E_{\rm tors} + E_{\rm vdw} + E_{\rm el} + E_{\rm cross}$$



$$E_{\rm str}(R^{\rm AB} - R_0^{\rm AB}) = k^{\rm AB}(R^{\rm AB} - R_0^{\rm AB})^2 = k^{\rm AB}(\Delta R^{\rm AB})^2$$

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

$$E_{\rm tors}(\omega) = \sum_{n=1}^{2} V_n \cos(n\omega)$$

$$E_{\rm coop}(\chi) = k^{\rm B}\chi^2 \quad \text{or} \quad E_{\rm coop}(d) = k^{\rm B}d^2$$

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

Problems with classical methods

Force field	Types	$E_{ m str}$	$E_{\rm bend}$	E_{oop}	$E_{ m vdw}$	$E_{ m el}$	$E_{ m cross}$	Molecules
AMBER	41	P2	P2	imp.	12–6 12–10	charge	none	proteins, nucleic acids, carbohydrates
CFF91/93/95	48	P4	P4	P2	9–6	charge	ss,bb,st, sb,bt,btb	general
CHARMM	29	P2	P2	imp.	12-6	charge	none	proteins
COSMIC	25	P2	P2		Morse	charge	none	general
CVFF	53	P2 or Morse	P2	P2	12–6	charge	ss,bb,sb, btb	general
DREIDING	37	P2 or Morse	P2(cos)	P2(cos)	12–6 or Exp–6	charge	none	general
EAS	2	P2	P3	none	Exp-6	none	none	alkanes
ECEPP		fixed	fixed	fixed	12–6 and 12–10	charge	none	proteins
EFF	2	P4	P3	none	Exp-6	none	ss,bb,sb, st,btb	alkanes
ENCAD	35	P2	P2	imp.	12–6	charge	none	proteins, nucleic acids
ESFF	97	Morse	P2(cos)	P2	9–6	charge	none	all elements

Problems with classical methods

MMFF	99	P4	P3	P2	14–7	charge	sb	general
MOMEC		P2	P2	P2	Exp–6	none	none	metal coordination
NEMO		fixed	fixed	none	Exp-6	quad, polar	none	special
OPLS	41	P2	P2	imp.	12-6	charge	none	proteins, nucleic
								acids,
								carbohydrates
PFF		P2	P2	imp.	12–6	polar	none	proteins
PROSA	41	P2	P2	imp.	12-6	polar	none	proteins
QMFF	32	P4	P4	P2	9–6	charge	ss,sb,st,bb,	general
							bt,btb	
SDFF		P4	P4		9–6	charge,	ss,st,tt	hydrocarbons
						dipole,		
						polar		
TraPPE		fixed	P2	fixed	12–6	charge	none	C, N, O
								compounds
TRIPOS	31	P2	P2	P2	12–6	charge	none	general
UFF	126	P2 or	$\cos(n\theta)$	imp.	12–6	charge	none	all elements
		Morse						
YETI	17	P2	P2	imp.	12-6 and	charge	none	proteins
					12-10			

Problems with classical methods

Force field	R_0 (Å)			k (mdyn/Å)				
	C—C	С—О	C—F	C=0	C—C	С—О	C—F	C=O
MM2	1.523	1.402	1.392	1.208	4.40	5.36	5.10	10.80
MM3	1.525	1.413	1.380	1.208	4.49	5.70	5.10	10.10
MMFF	1.508	1.418	1.360	1.222	4.26	5.05	6.01	12.95
AMBER	1.526	1.410	1.380	1.220	4.31	4.45	3.48	8.76
OPLS	1.529	1.410	1.332	1.229	3.73	4.45	5.10	7.92

Reading exercise

Jensen

Chapter 2: Force-field methods

Back to description of molecular systems



Is the system completely described yet?

0	-0.60345	0.43840	0.45675	R1 = 0.96
н	0.36444	0.39261	0.46442	R2 = 0.96
Н	-0.88229	-0.47684	0.61017	A = 104.5

Back to description of molecular systems



Problem 1: What is the number of electrons in the system?

Problem 2: Are there multiple ways of "filling" the molecule with electrons? If yes, how to handle this problem?

Back to description of molecular systems



Problem 1: What is the number of electrons in the system? Solution: Specify the charge explicitly

Problem 2: Are there multiple ways of "filling" the molecule with electrons? If yes, how to handle this problem? Solution: Specify the "spin multiplicity" explicitly (brute force)

Over-simplified picture



Upadhyay et al., Molecular Catalysis,

2023



27



Upadhyay et al., Molecular Catalysis, 2023



Reaction Coordinate

Reaction Coordinate

Upadhyay et al., Molecular Catalysis, 2023



Upadhyay et al., Molecular Catalysis, 2023

Reaction Coordinate













		! Initial Par ! (Angstroms and	ameters ! Degrees) !	
! Name	Definition	Value	Derivative Info.	!
! R1 ! R2 ! A1	R(1,2) R(1,3) A(2,1,3)	0.9671 0.9671 104.9567	estimate D2E/DX2 estimate D2E/DX2 estimate D2E/DX2	! ! !
		! Optimized Pa ! (Angstroms and	rameters ! Degrees) !	
	Definition	! Optimized Pa ! (Angstroms and Value	rameters ! Degrees) ! Derivative Info.	 !

	Item	Value	Threshold	Converged?
Maximum	Force	0.008402	0.000450	NO
RMS	Force	0.006861	0.000300	NO
Maximum	Displacement	0.011720	0.001800	NO
RMS	Displacement	0.010727	0.001200	NO
Predicte	ed change in H	Energy=-1.308751D	-04	

	Item	Value	Threshold	Converged?		
Maximum	Force	0.000028	0.000450	YES		
RMS	Force	0.000017	0.000300	YES		
Maximum	Displacement	0.000098	0.001800	YES		
RMS	Displacement	0.000101	0.001200	YES		
Predicted change in Energy=-2.567564D-09						
Optimization completed.						
Stationary point found						

	A1	A1	B2
Frequencies	1627.9274	3891.8284	4000.3230
Red. masses	1.0832	1.0447	1.0827
Frc consts	1.6913	9.3230	10.2083
	А	А	А
Frequencies	-2129.5184	12.0423	15.7236
Red. masses	1.0975	7.0535	4.3743
Frc consts	2.9323	0.0006	0.0006



213 vibrational frequencies; only and exactly 1 negative!



Some terms to know, remember and understand

- Steepest decent
- Conjugate gradient
- Intrinsic reaction coordinate (IRC)
- Climbing image nudged elastic band (CI-NEB)
- Quasi-Newton synchronous transit (QST)

Reading exercise Lewars Computational Chemistry

Chapter 2: The concept of potential energy surface



Wave-particle duality



Wave-particle duality



Wave-particle duality



Schroedinger equation

$$\mathtt{i} \mathtt{h} \frac{\partial}{\partial \mathtt{t}} \Psi(\mathtt{x}, \mathtt{t}) = -\frac{\mathtt{h}^2}{2\mathtt{m}} \frac{\partial^2}{\partial \mathtt{x}^2} \Psi(\mathtt{x}, \mathtt{t}) + \mathtt{V}(\mathtt{x}, \mathtt{t}) \Psi(\mathtt{x}, \mathtt{t})$$

Hamiltonian operator

$$\begin{split} \hat{\mathbf{H}} &= -\frac{\hbar^2}{2\mathrm{m}} \nabla^2 + \mathbf{V}(\mathbf{x}) \\ & \mathbf{\hat{H}} \psi = \mathbf{E} \psi \end{split}$$

Schroedinger equation – Particle in an infinite 1-D well



Schroedinger equation – Particle in an infinite 1-D well



Schroedinger equation – Particle in an infinite 1-D well



The electronic structure problem

 $\hat{H}\Psi_{i}(\vec{x}_{1},\vec{x}_{2},...,\vec{x}_{N},\vec{R}_{1},\vec{R}_{2},...,\vec{R}_{M}) = E_{i}\Psi_{i}(\vec{x}_{1},\vec{x}_{2},...,\vec{x}_{N},\vec{R}_{1},\vec{R}_{2},...,\vec{R}_{M})$

 $\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{i>i}^{N} \frac{1}{r_{ii}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$ $\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{i>i}^{N} \frac{1}{r_{ii}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$ $E_{nuc} = \sum_{nuc}^{M} \sum_{nuc}^{M} \frac{Z_A Z_B}{n}$

The electronic structure problem

Quantity	Atomic unit	Value in SI units	Symbol (name)
mass	rest mass of electron	9.1094 x 10^{-31} kg	m_e
charge	elementary charge	1.6022 x 10^{-19} C	e
action	Planck's constant/ 2π	1.0546 x 10^{-34} J s	\hbar
length	$4\pi\epsilon_0 \hbar / m_e e^2$	5.2918 x 10^{-11} m	a_0 (bohr)
energy	$\hbar^2 / m_e a_0^2$	4.3597 x 10^{-18} J	E_h (hartree)

Solution of hydrogen atom



Solution of hydrogen atom

$$\begin{aligned} -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V(r)\psi &= E\psi \\ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) Y(\theta, \phi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) R(r) Y(\theta, \phi) \\ &+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} R(r) Y(\theta, \phi) - \frac{2m}{\hbar^2} \left[V(r) - E \right] R(r) Y(\theta, \phi) = 0 \\ \Rightarrow \quad Y(\theta, \phi) \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) + R(r) \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) \\ &+ R(r) \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) - \frac{2m}{\hbar^2} \left[V(r) - E \right] R(r) Y(\theta, \phi) = 0 \end{aligned}$$

Solution of hydrogen atom

$$\begin{split} \left\{ \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) - \frac{2mr^2}{\hbar^2} \Big[V(r) - E \Big] \right\} \\ &+ \left[\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) \Big] = 0 \\ &\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2mr^2}{\hbar^2} \Big[V(r) - E \Big] = l(l+1) \\ &\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) = -l(l+1) \end{split}$$

Solution of hydrogen atom

$$R_{1,0}(r) = 2a_0^{-3/2}e^{-r/a_0}$$

$$R_{2,0}(r) = \frac{1}{\sqrt{2}}a_0^{-3/2}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$R_{2,1}(r) = \frac{1}{\sqrt{24}}a_0^{-3/2}\frac{r}{a_0}e^{-r/2a_0}$$

$$R_{3,0}(r) = \frac{2}{\sqrt{27}}a_0^{-3/2}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$$

$$R_{3,1}(r) = \frac{8}{27\sqrt{6}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$$

$$R_{3,2}(r) = \frac{4}{81\sqrt{30}}a_0^{-3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}$$

54

N-electron wavefunction approximation – Slater determinant

$$\begin{split} \Psi_0 &= \chi_1(\vec{x}_1) \ \chi_2(\vec{x}_2) \dots \chi_i(\vec{x}_i) \ \chi_j(\vec{x}_j) \cdots \chi_N(\vec{x}_N) \\ \Psi_0 &\approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \\ \chi(\vec{x}) &= \phi(\vec{r}) \ \sigma(s), \ \sigma &= \alpha, \beta \end{split}$$

Basis functions

Slater-type orbitals

$$\varphi_{i}(\xi, n, l, m; r, \theta, \varphi) = Nr^{n-1}e^{-\xi r}Y_{lm}(\theta, \varphi)$$
$$\varphi_{1s} = \left(\frac{\xi_{1}^{3}}{\pi}\right)^{1/2} \exp(-\xi_{1}r)$$
$$\varphi_{2s} = \left(\frac{\xi_{2}^{5}}{96\pi}\right)^{1/2} r \exp\left(-\frac{\xi_{2}r}{2}\right)$$
$$\varphi_{2p_{x}} = \left(\frac{\xi_{2}^{5}}{32\pi}\right)^{1/2} x \exp\left(-\frac{\xi_{2}r}{2}\right)$$

Gaussian-type orbitals

$$g(\alpha, l, m, n; x, y, z) = Ne^{-\alpha r^{2}} x^{l} y^{m} z^{n}$$

$$g_{x}(\alpha, r) = \left(\frac{128\alpha^{5}}{\pi^{3}}\right)^{1/4} x \exp(-\alpha r^{2})$$

$$g_{xx}(\alpha, r) = \left(\frac{2048\alpha^{7}}{9\pi^{3}}\right)^{1/4} x^{2} \exp(-\alpha r^{2})$$

$$g_{xy}(\alpha, r) = \left(\frac{2048\alpha^{7}}{\pi^{3}}\right)^{1/4} xy \exp(-\alpha r^{2})$$

Basis functions



Basis functions

Double zeta

Minimal basis sets and contracted Gaussians: STO-nG

Split-valence basis sets: 6-31G

Split-valence with polarisation functions: 6-31G(d,p)

Split-valence with diffuse functions: 6-31+G(d)

6-311++G(3df,3pd)

Basis functions

6-31+G*

19

		Basis set	# functions	6	
		STO-3G	5		
		3-21G	9		
		4-31G	9		
Basis set	# fund	ctions		Basis set	# functions
6-31G	9			6-311G	13
6-31G*	15			6-311G*	18

59

22

6-311+G*

Variational principle

$$\left\langle \Psi_{\text{trial}} \left| \hat{H} \right| \Psi_{\text{trial}} \right\rangle = E_{\text{trial}} \ge E_0 = \left\langle \Psi_0 \left| \hat{H} \right| \Psi_0 \right\rangle$$

Reading exercise Levine Quantum Chemistry

Chapter 6: The Hydrogen atom

Chapter 8 The variational method

Koch and Holthausen A Chemist's Guide to Density Functional Theory

Chapter 1: Elementary quantum chemistry