

Lecture 7

Tight-binding and semiempirical approaches

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Outline

- Methodology
- Non-self-consistent methods (wrt e-e interaction mean field)
 - Tight binding (TB) methods
 - Effective many-body Hamiltonians
- Self-consistent methods
 - Density functional tight binding (DFTB)
 - Semiempirical methods

Reminder: The electronic structure problem

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} \right] \psi_e(\mathbf{r}; \mathbf{R}) = E_e \psi_e(\mathbf{r}; \mathbf{R})$$

- Electrons interacting via Coulomb potential in electrostatic field of nuclei
- **Problem 1** – one-electron problem: use finite basis set (atomic-like orbitals STO/GTO or plane waves)
- **Problem 2** – many-body problem: use mean field (HF, DFT, TDDFT) and perturbation theories (MP2, CI, CC) in Fock space (basis of Slater determinants)

<i>Method</i>	<i>Explicit e-correlations</i>	<i>Wave-function</i>	<i>Cost (PC)</i>
<i>Ab initio</i> (MP2, CI, CAS-CI, CC-EOM)	<i>All</i> (depends on level of theory)	<i>Exact</i> (for given basis set)	<i>Large</i> (≥10 electrons)
<i>Density Functional</i> (DFT, TDDFT)	<i>Dynamic only</i>	<i>Kohn-Sham</i> (a single-det. “fit” to e-density)	<i>Significant</i> (≤1000 atoms)
<i>Semiempirical</i> (AM1, PM7, ZINDO)	<i>Coulomb, exchange, static</i>	<i>Hartree-Fock</i> (variationally optim. single-det.)	<i>Low</i> (≤10 000 atoms)
<i>Tight-binding</i> (Huckel, Frenkel, DFTB)	<i>No</i>	<i>One-electron</i> (full e-energy is inaccurate)	<i>Approach MM</i> (>10 000 atoms)

Methodology: reducing 1e&MB basis

- Many codes use all-electron basis

1) Reduce number of electrons

- Pseudopotentials

2) Reduce number of one-electron orbitals but fit the model

Hamiltonian(geometry), total energy(geometry)

- Semiempirical – NDDO
- SCC-DFTB – small electron density fluctuations
- *Many-body basis is also reduced by neglecting 3c/4c integrals*

3) No SCF in addition (no explicit ee-interaction) → nontransferable

- TB – no reliable implementations for accurate total energy
- Effective Hamiltonian – small geometry deviations
- Coarse graining – rigid fragments

Parameterization is the bottleneck of fitted models

Historical TB models

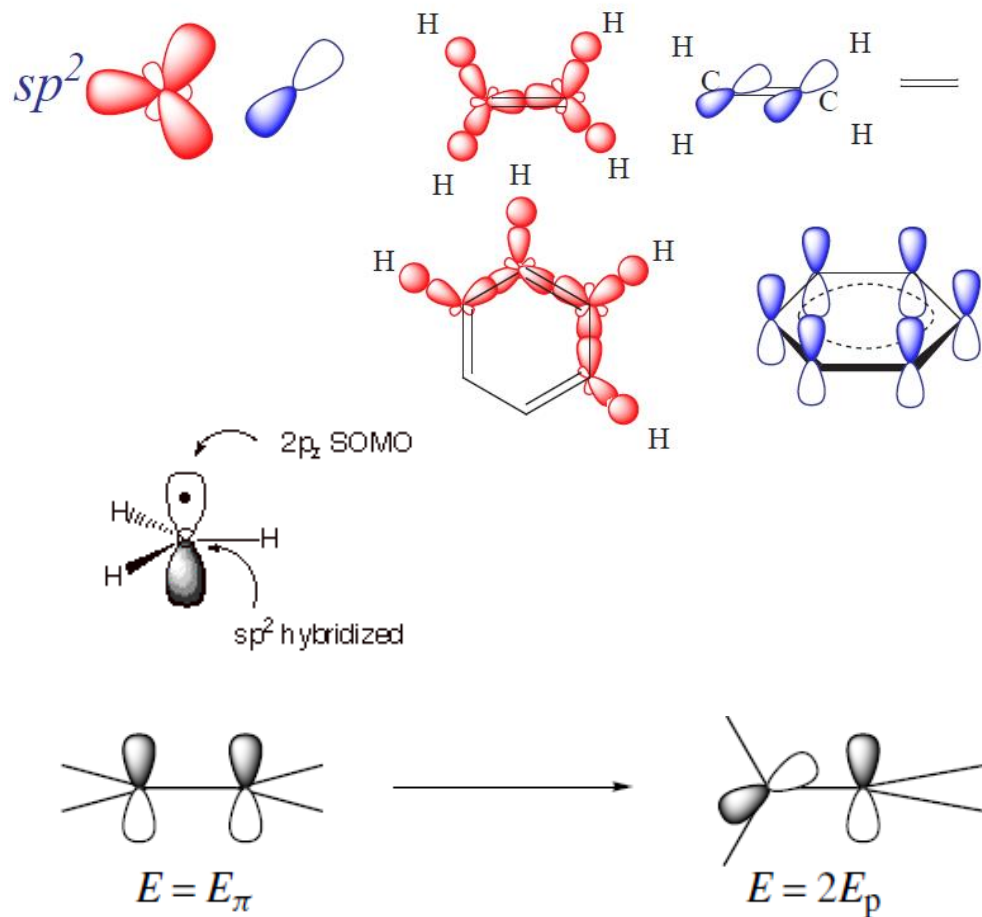
- Huckel model of π -conjugated hydrocarbons
- PPP model of π -conjugated hydrocarbons
- SSH model of polyacetylene

- Slater-Koster parameters for semiconductors

The Huckel approximation

An example of tight-binding Hamiltonian, first constructed by Erich Huckel in 1930 for aromatic hydrocarbons

- 1) Only π -orbitals (one per carbon, the blue color) are considered
- 2) The orbitals are orthogonal $S_{ij} = \delta_{ij}$
- 3) Diagonal resonance term $H_{ii} = \alpha$ is derived from the ionization potential of methyl radical.
- 4) Off-diagonal nearest neighbor resonance terms are also derived from experimental data: $E_p = \alpha$ and $E_\pi = \alpha + 2\beta$
- 5) Not nearest-neighbor resonance interactions are neglected!



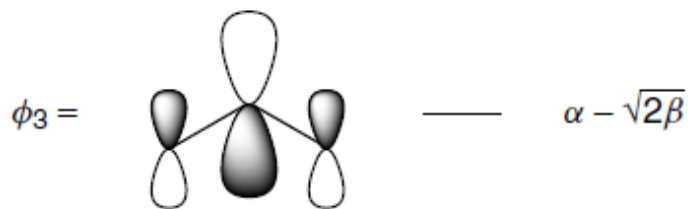
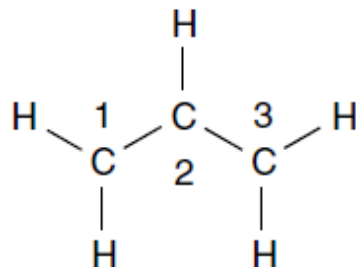
Very simple model correctly describing physics of π -conjugated molecules and solids

Huckel approach to hydrocarbons

The allyl system, following Cramer

The secular equation:

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

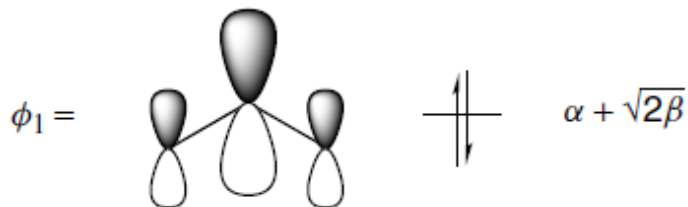
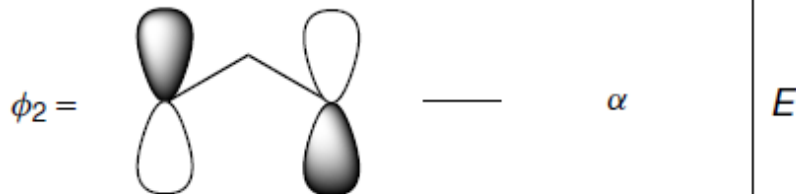


Eigenvalues correspond to bonding, non-bonding and anti-bonding molecular orbitals:

$$E = \alpha + \sqrt{2}\beta, \quad \alpha, \quad \alpha - \sqrt{2}\beta$$

The bonding (lowest energy) MO

$$\phi_1 = \frac{1}{2}p_1 + \frac{\sqrt{2}}{2}p_2 + \frac{1}{2}p_3$$



2 electrons per orbital starting from the bottom!

π -bonding energy of the system:

allyl cation (2e) $2(\alpha + \sqrt{2}\beta)$

allyl radical (3e) $2(\alpha + \sqrt{2}\beta) + \alpha$

allyl anion (4e) $2(\alpha + \sqrt{2}\beta) + 2\alpha$

Figure 4.2 from Cramer: Huckel MOs for the allyl system

PPP (Pariser-Parr-Pople) model

Simple model with ee-interaction (1953)

Again, only π -electrons are considered, but let add to the SSH form simple Coulomb interactions (only diagonal elements in the tetradic matrix V)

$$\langle mk|nl\rangle = V_{mn}\delta_{mk}\delta_{nl}$$

$$V_{nm} = \frac{U}{\sqrt{1 + (r_{nm}/a_o)^2}} \quad \text{Ohno form}$$

$$t_{nn} = \sum_m V_{nm} \quad \text{Diagonal terms}$$

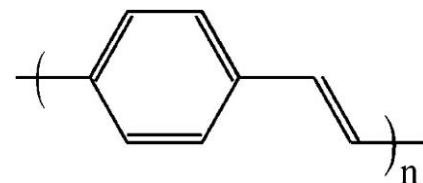
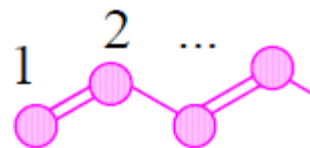
$$t_{n,n\pm 1} = \beta_0 - \beta_1 l_n \quad \text{Transfer integrals}$$

$$V(\bar{\rho})_{mn} = -V_{mn}\bar{\rho}_{mn} + 2\delta_{mn} \sum_l V_{ml}\bar{\rho}_{ll}$$

$$\hat{\mu}_{nm} = ez_n\delta_{nm} \quad \text{Dipole matrix}$$

J.A. Pople and W. Kohn: Nobel Prize in chemistry (1998) for quantum chemistry (DFT and electronic structure)

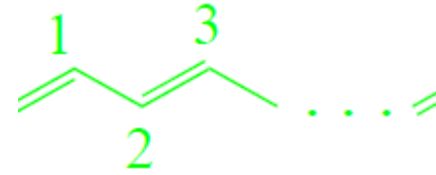
$$\hat{H}_e = \sum_{mn}^K t_{mn}c_m^+c_n + \frac{1}{2} \sum_{mnkl}^K V_{nm,kl}c_m^+c_n^+c_kc_l$$



- Conceptually simple – only 1 basis function per atom (good parameterization exist at least for C, N and O);
- Electron-electron interactions are accounted for at some qualitative level;
- No σ -bonding, no optimal geometries;
- No analytical and numerical solutions exist for solving Schrodinger equation – many-electron effects!
- Within Hartree-Fock approximation, diagonalization of the Fock operator includes iterative numerical SCF procedure;
- Correlated excited states can be further obtained using subsequent CI calculations

SSH (Su-Schrieffer-Heeger) model

Simple model with ep-interaction (1979)



Solitons in conducting polymers

A. J. Heeger S. Kivelson J. R. Schrieffer W.-P. Su

Reviews of Modern Physics, Vol. 60, No. 3, July 1988

$$H_{\text{SSH}} = H_{\pi} + H_{\pi\text{-ph}} + H_{\text{ph}}$$

← Total Hamiltonian

$$H_{\pi} = -t_0 \sum_{n,s} (c_{n+1,s}^{\dagger} c_{n,s} + c_{n,s}^{\dagger} c_{n+1,s})$$

← Huckel part for π -electrons

$$H_{\pi\text{-ph}} = \alpha \sum_{n,s} (u_{n+1} - u_n) (c_{n+1,s}^{\dagger} c_{n,s} + c_{n,s}^{\dagger} c_{n+1,s})$$

← Electron-phonon coupling

$$H_{\text{ph}} = \sum p_n^2 / 2M + K / 2 \sum (u_{n+1} - u_n)^2$$

← Phonon part

Solutions of the Hamiltonian in a form of Bloch functions:

$$c_{ks} = (N^{-1/2}) \sum_{n,s} \exp(-ikna) c_{ns}$$

A.J. Heeger, A.J. MacDiarmid, H. Shirakawa:
Nobel Prize in chemistry (2000) for discovery
of conducting polymers

Diagonalized Hamiltonian:

$$H(u) = \sum [\epsilon_k (c_{ks+}^{\dagger} + c_{ks+} - c_{ks-}^{\dagger} - c_{ks-}) + \Delta_k (c_{ks+}^{\dagger} + c_{ks-} + c_{ks-}^{\dagger} - c_{ks+})] + 2NKu^2$$

$$\Delta_k = 4\alpha u \sin ka \quad \text{Energy gap parameter}$$

$$\epsilon_k = 2t_0 \cos ka \quad \text{Band energy}$$

Tight binding for solids: NRL developments

- Parameterized for
 - band structure [Phys Rev 94, 1498 (1954)]
 - “band energy = total energy” calculations [Phys Rev B 50, 14694 (1994)]
- Transferable between different structures of the same compound

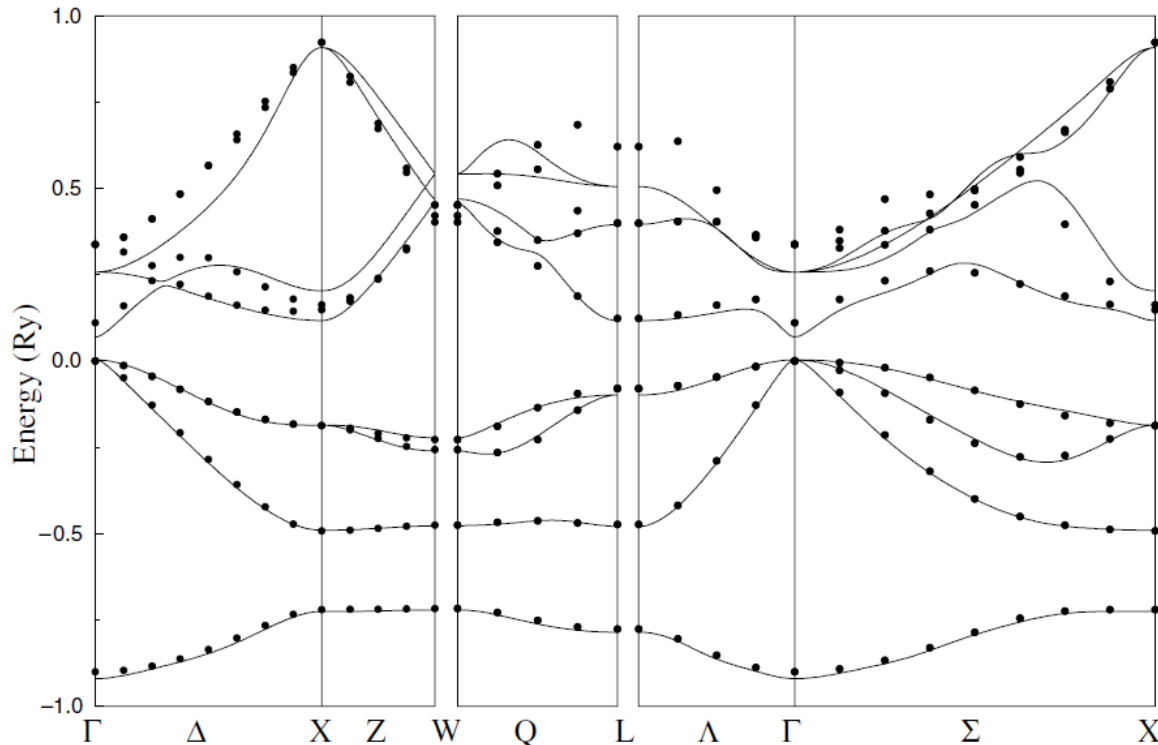


Figure 3. Comparison of an empirical pseudopotential band structure of GaAs (dots) to the band structure obtained by SK parametrization (solid curve).

Orthogonal vs nonorthogonal

Orthogonal

- More convenient for orbital analysis and 2nd quantization
- Majority of theoretical models, MOPAC
- NBO and usually LMO

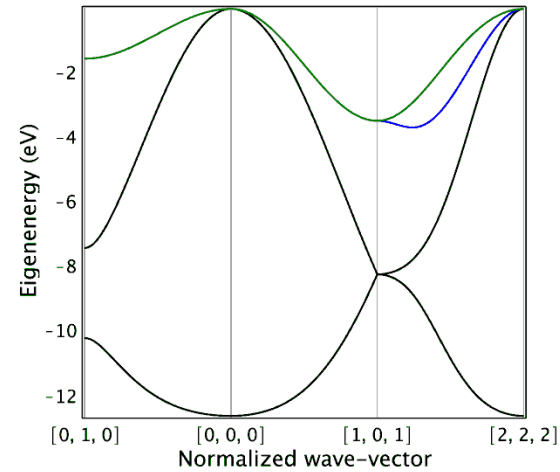
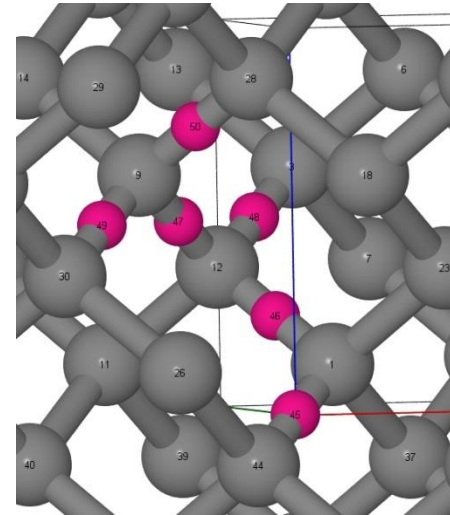
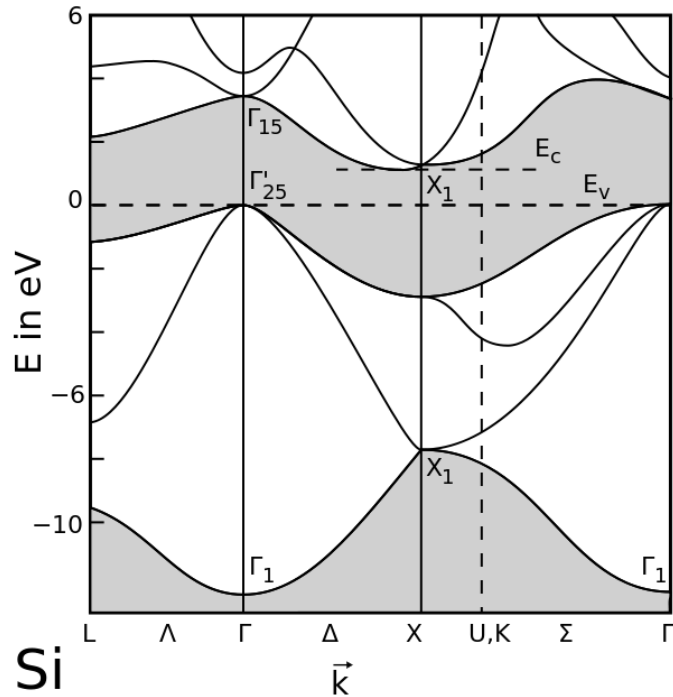
Nonorthogonal

- More compact in space, more transferable
- NRL tight-binding, DFTB

Conversion

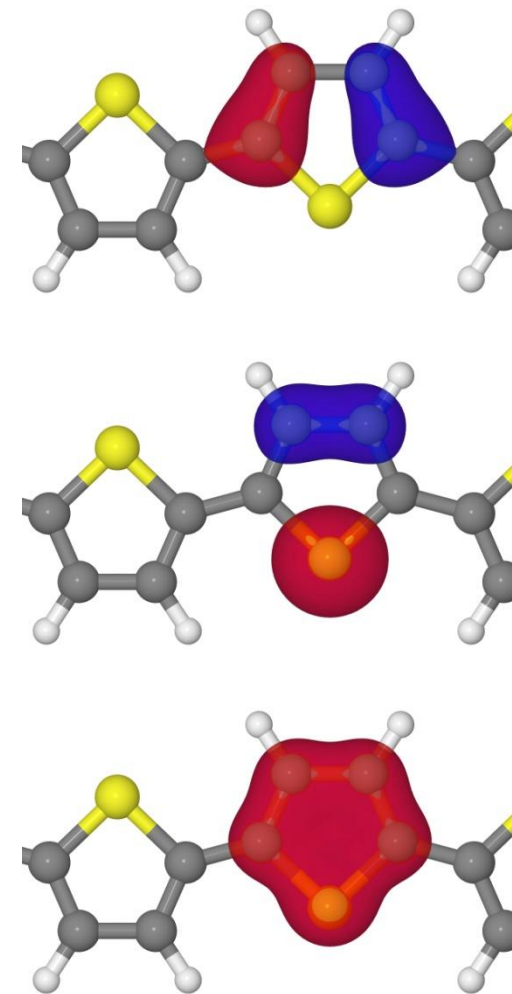
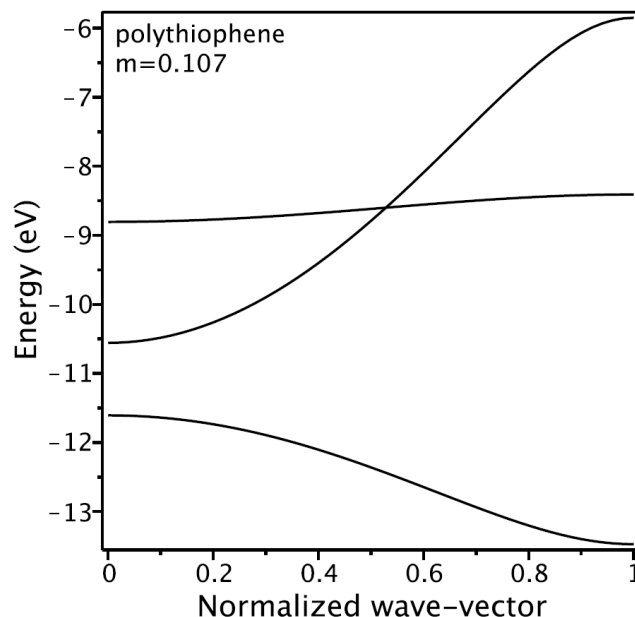
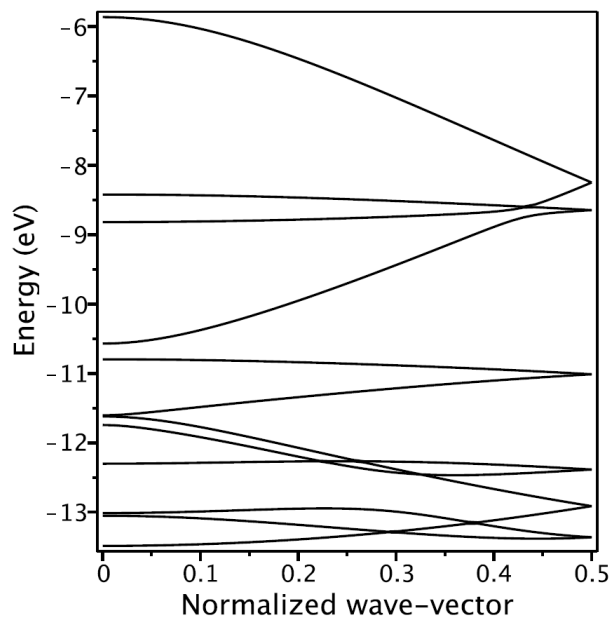
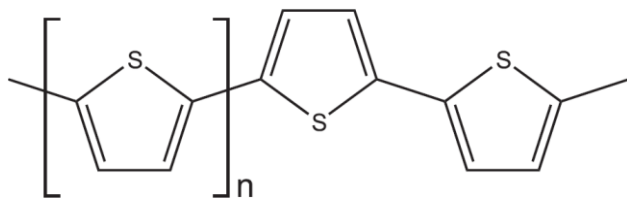
- Symmetric (Lowdin) orthogonalization $H' = S^{-1/2}HS^{-1/2}$
nearest neighbor \rightarrow exponentially fading transfer integrals

Example: 6-parameter model of Si VB



Also can be used for band structure if calculation of each k-point is demanding – extrapolation in real space is often much more efficient than interpolation in k-space

Coarse graining for molecular systems



Advantage: DFT accuracy at TB computational complexity

Challenges: total energy, large molecular deformations

Complex polymer: Chem Sci 8, 1146 (2017)

Complex molecular solid: Chem Mater 33, 966 (2021)

Holstein-Peierls Hamiltonian

Ann Phys 8, 32 (1959), J Chem Phys 83, 1854 (1985)

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_{\alpha} \hbar\omega_{\alpha} \left(b_{\alpha}^\dagger b_{\alpha} + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_{\alpha} g_{ij\alpha} \left(b_{\alpha}^\dagger + b_{\alpha} \right) c_i^\dagger c_j$$

here c_i – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian, b_{α} – normal modes or phonons,

$$H_{ij}^{1p} = \delta_{ij} \varepsilon_i + (1 - \delta_{ij}) t_{ij},$$

ε_i – onsite energy, t_{ij} – transfer integral, $g_{ij\alpha}$ – electron-phonon coupling (local for $i = j$, nonlocal otherwise)

Approximations:

- mean field approximation for electrons
- linear electron-phonon coupling
- harmonic approximation for atomic motion

Most of many-body Hamiltonians are tractable only in the minimal basis

Discussion

1. Why the same values of TB parameters cannot be used for different states (neutral, charged, triplet, excited)?
2. In which cases the same set of geometry-dependent TB parameters can be used (cannot be used) to compare different polymorphs of the same material? Give examples.
3. What will be the smallest basis set for CH₄ molecule?
4. Write the simplest TB Hamiltonian for VB of CH₄ molecule. Write its basis set in terms AOs of C and H.

Self-consistent methods

- **Density functional tight binding (DFTB)**
(minimal AO basis + simplified orbital-free density functional, parameterized with local functional and empirical dispersion)
- **Semiempirical methods**
(minimal AO basis + neglecting majority of multicenter integrals, parameterized for HF energy including support of fractional occupations and CI wave-function)

DFTB – Density Functional Tight Binding

- Tight-binding + simplified (orbital-free) density functional

$$E = \sum_a f_a \sum_{\mu\nu} c_{\mu}^{a*} c_{\nu}^a H_{\mu\nu}^0 + \frac{1}{2} \sum_{IJ} \gamma_{IJ}(R_{IJ}) \Delta q_I \Delta q_J + \sum_{I < J} V_{\text{rep}}^{IJ}(R_{IJ})$$

$$H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_K (\gamma_{IK} + \gamma_{JK}) \Delta q_K, \quad \mu \in I \quad \nu \in J$$

- Parameterized by higher level of theory (DFT)
 - Self-consistent (SCC DFTB) wrt electronic density fluctuations
1. P Koskinen, V Mäkinen, Density-functional tight-binding for beginners, *Comp Mater Sci* 47, 237 (2009)
 2. [DFTB+](#), a software package for efficient approximate density functional theory based atomistic simulations, *J Chem Phys* 152, 124101 (2020)
 3. [GFN2-xTB](#) – An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions, *J Chem Theory Comput* 15, 1652 (2019)

■ About DFTB+

• Features

■ Download

■ Documentation

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■ Developer pages

Features

The latest [stable release](#) has among others, the following capabilities:

- Non-scc and scc calculations for clusters and periodic systems (with arbitrary K-point sampling)
- Spin polarized calculations with colinear and non-colinear spin
- Dispersion correction (D3, D4, many-body and Tkatchenko-Scheffler)
- 3rd order correction and other DFTB3-features
- Ability to treat f-electrons
- LDA+U (DFTB+U) extension
- Spin orbit coupling
- Pseudo self interaction correction
- Various types of external electrical fields, QM/MM coupling via fields
- Time dependent DFTB in the Casida-formulation
- Range separated ground state calculations and excited state calculations for spin free singlet systems
- Real time electronic and coupled electron-ion Ehrenfest dynamics
- REKS (spin-Restricted Ensemble Kohn-Sham) calculations for ground and low-lying excited states
- Delta DFTB for lowest singlet excited state
- Electron transport calculation via non-equilibrium Greens function technique (also for systems with colinear spin)
- Phonon transport calculations
- Particle-particle random-phase approximation (pp-RPA) for calculation of suitable excitations
- Extended Lagrangian Born-Oppenheimer MD (XLBOMD)
- Several implicit solvation models
- Helical geometries supported for non-SCC calculations
- Geometry and lattice optimisation
- Vibrational frequency calculation.
- Molecular dynamics (NVE, NPH, NVT and NPT ensembles)
- Support for meta-dynamics in MD via the Plumed library,
- MPI- and OpenMP parallelisation
- Usage of GPU for diagonalisation
- Using DFTB+ via sockets
- DFTB+ can be compiled as a library and linked to simulation packages.
- Automatic code validation (autotest system)
- User friendly, extensible input format (HSD)
- Additional tool for generating cube files for charge distribution, molecular orbitals, etc. (Waveplot)

DFTB: approaching DFT accuracy at MLIP speed

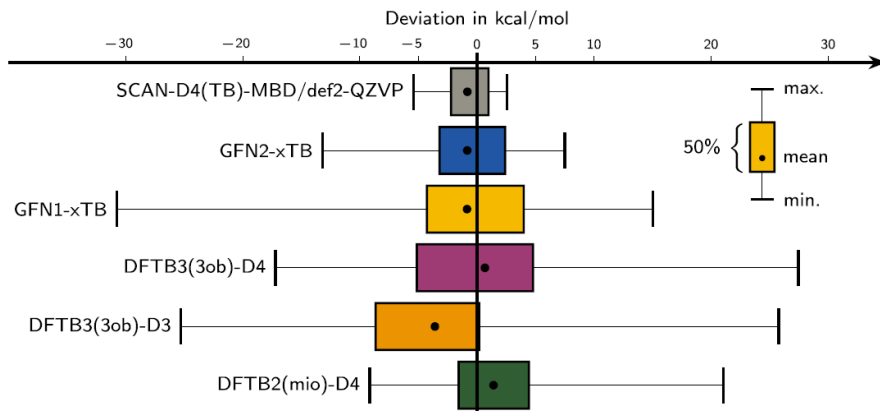
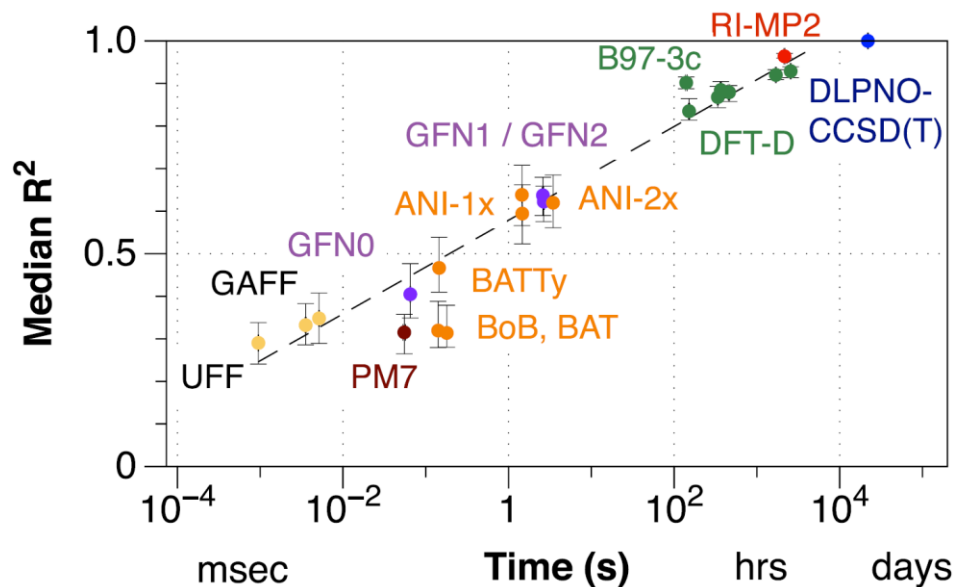


FIG. 1. Performance of different dispersion corrected tight binding methods on the S30L benchmark set, and the values for SCAN-D4 are taken from Ref. 65.

J. Chem. Phys. 152, 124101 (2020); doi: 10.1063/1.5143190

152, 124101-6



Int J Quantum Chem 121, e26381 (2021);
doi:10.1002/qua.26381

DFTB is the best universal approach to systems of 1000s of atoms

NDDO – foundation of semiempirical methods

Main idea – minimize basis \rightarrow

- 1) One AO per valence electron + polarization orbitals
- 2) NDDO = Neglect of Diatomic Differential Overlap:

$$\overline{\phi_\alpha(x)\phi_{\alpha'}(x)\phi_{\beta'}(y)\phi_\beta(y)} = 0$$

if either α and α' or β and β' do not belong to one center.

- Approximation leading to a neglect of many integrals (all 3c/4c-integrals, and 2c-exchange), partially compensated by fitting of the rest of terms to the reference data!
- Basis set is considered orthogonal by construction.
- Usually limited to Hartree-Fock and post-HF (MOPAC).

$$\hat{H}_e = \sum_{mn} t_{mn} c_m^+ c_n + \frac{1}{2} \sum_{mnkl} V_{nm,kl} c_m^+ c_n^+ c_k c_l$$

Calculating and storing all V_{nmkl} is computationally demanding

Example: MNDO, AM1, PM3, PM7 methods

$$h_{\mu\nu} = \langle \mu_A | \mathbf{h} | \nu_B \rangle = \delta_{\mu\nu} U_\mu - \sum_{a \neq A}^{N_{\text{nuclei}}} Z'_a \langle \mu_A \mu_A | \nu_A \nu_A \rangle \quad \text{t-term!}$$

$$U_\mu = \langle \mu_A | -\frac{1}{2} \nabla^2 - \mathbf{V}_A | \nu_A \rangle$$

$$\langle \mu_A | \mathbf{h} | \nu_B \rangle = \frac{1}{2} S_{\mu\nu} (\beta_\mu + \beta_\nu)$$

$$\langle ss | ss \rangle = G_{ss}$$

$$\langle sp | sp \rangle = G_{sp}$$

$$\langle ss | pp \rangle = H_{sp}$$

$$\langle pp | pp \rangle = G_{pp}$$

$$\langle pp' | pp' \rangle = G_{p2}$$

V-term
for a
single
center

+ ~22 parameters
composing V-term
for 2 centers!

See <http://openmopac.net/manual/parameters.html>

How accurate is NDDO?

Exact for 2c2e problem and is used in most of quantum chemistry and condensed matter theory models (PPP, extended Hubbard)

The full Hamiltonian matrix is given by

$$H = \begin{pmatrix} 2\varepsilon_1^0 + 2\Lambda_{121} + W_{11} & s\varepsilon_1^0 + s\Lambda_{121} + t^0 + W_{112} & s\varepsilon_1^0 + s\Lambda_{121} + t^0 + W_{112} & 2st^0 + W_{12}^{\text{ex}} \\ \dots & \varepsilon_1^0 + \varepsilon_2^0 + \Lambda_{121} + \Lambda_{212} + W_{12} & 2st^0 + W_{12}^{\text{ex}} & s\varepsilon_2^0 + s\Lambda_{212} + t^0 + W_{122} \\ \dots & \dots & \varepsilon_1^0 + \varepsilon_2^0 + \Lambda_{121} + \Lambda_{212} + W_{12} & s\varepsilon_2^0 + s\Lambda_{212} + t^0 + W_{122} \\ \dots & \dots & \dots & 2\varepsilon_2^0 + 2\Lambda_{212} + W_{22} \end{pmatrix}$$

This Hamiltonian can be written in a compact ZDO form

$$H = \begin{pmatrix} 2\varepsilon_1 + U_1 & s\varepsilon_1 + t_{12} & s\varepsilon_1 + t_{12} & 2st_{12} \\ \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & 2st_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \varepsilon_1 + \varepsilon_2 + V_{12} & s\varepsilon_2 + t_{12} \\ \dots & \dots & \dots & 2\varepsilon_2 + U_2 \end{pmatrix}$$

with the renormalized parameters

$$\begin{aligned} \varepsilon_1 &= \varepsilon_1^0 + \Lambda_{121} + \frac{2sW_{112} - W_{12}^{\text{ex}}}{2s^2}, & U_1 &= W_{11} - \frac{2sW_{112} - W_{12}^{\text{ex}}}{s^2}, \\ \varepsilon_2 &= \varepsilon_2^0 + \Lambda_{212} + \frac{2sW_{221} - W_{12}^{\text{ex}}}{2s^2}, & U_2 &= W_{22} - \frac{2sW_{221} - W_{12}^{\text{ex}}}{s^2}, \\ t_{12} &= t_{12}^0 + \frac{W_{12}^{\text{ex}}}{2s}, & V_{12} &= W_{12} + \frac{W_{12}^{\text{ex}} - sW_{112} - sW_{221}}{s^2}. \end{aligned}$$

The semiempirical world in details

- Provides conceptually simple, compact and physically transparent Hamiltonian model;
- Parameterization is ALWAYS bound to the specific electronic structure level (e.g., Hartree-Fock approximation), but post-HF is meaningful
- Parameterization is subject to the fit to a reference data set;
- Semiempirical models cannot reproduce phenomena beyond their capacity (e.g. no Rydberg states);
- Generally good results are achieved only for the first and second rows elements (dynamic correlations with d-electrons are 'problematic');
- Semiempirical models are nice 'toys' – numerically easy and simple, but still true 'atomistic' approaches – always a good starting point for any electronic structure simulations ('testing the ground').
- Old models (currently obsolete): CNDO, INDO/1, INDO/2, NDDO
- Older models for ground state properties: MNDO, AM1, PM3
- Newer models for ground state properties: RM1, PM6, PM7 (variations with dispersive corrections)
- Older model for excited state properties: INDO/S=ZINDO
- Parameterization of d-electrons (so-so performance): MNDO-d, AM1-d, PM3-d, INDO/S, SINDO1.
- Semiempirical codes: MOPAC, AMPAC, SQM (MNDO...PM6), ZINDO, PySeQM. Also implemented in Gaussian, Turbomole, GAMESS...

Performance of PM7 semiempirical method

Heat of formation $\Delta H_f(\text{molecule}) = E_{\text{elec}}(\text{molecule}) - \sum^{M_{\text{atoms}}} E_{\text{elec}}(\text{atoms}) - \sum^{M_{\text{atoms}}} \Delta H_f(\text{atoms})$

Table 3.1 (from Jensen) Average heat of formation error (kJ/mol)

Compounds	Number of compounds	MNDO	AM1	PM3
H, C, N, O	276	77	44	33
F	133	352	207	47
Si	78	96	87	59
All normal valent	607	102	62	47
Hypervalent	106	437	261	72
All	713	193	116	49

1 eV = 23.0606 kcal/mol 1kcal/mol = 4.184kJ/mol kT(300K) ~ 25meV

Table 3.2 (from Jensen) Average errors in bond distances (Å)

Bond to:	MNDO	AM1	PM3
H	0.015	0.006	0.005
C	0.002	0.002	0.002
N	0.015	0.014	0.012
O	0.017	0.011	0.006
F	0.023	0.017	0.011
Si	0.030	0.019	0.045

See http://openmopac.net/PM7_accuracy/PM7_accuracy.html

Usage 1: Static e-e correlations

Use for preliminary analysis of the wave-function
and to find low-energy states

Table: Use of OPEN (<i>n, m</i>)					
UHF Keywords	RHF Keywords	Example	Number of M.O.s	No. of Electrons	State
MS=1	OPEN (2, 2)	Twisted Ethylene	2	2	3A_2
OPEN (1, 2)	OPEN (1, 2)	O_2^+	2	1	$^2\pi_g$
MS=-0.5 OPEN (2, 3)	OPEN (5, 3)	CH_4^+	3	5	2T_2
MS=1.5	OPEN (3, 3)	$[Cr^{III}F_6]^{3-}$	3	3	$^4A_{2g}$
MS=2.5	OPEN (5, 5)	$[Mn^{II}(H_2O)_6]^{2+}$	5	5	6A_1
MS=-0.5 OPEN (2, 3)	OPEN (5, 3)	$[Fe^{III}(CN)_6]^{3-}$	3	5	$^2T_{2g}$

See <http://openmopac.net/manual/open.html>

Usage 2: Nonadiabatic molecular dynamics

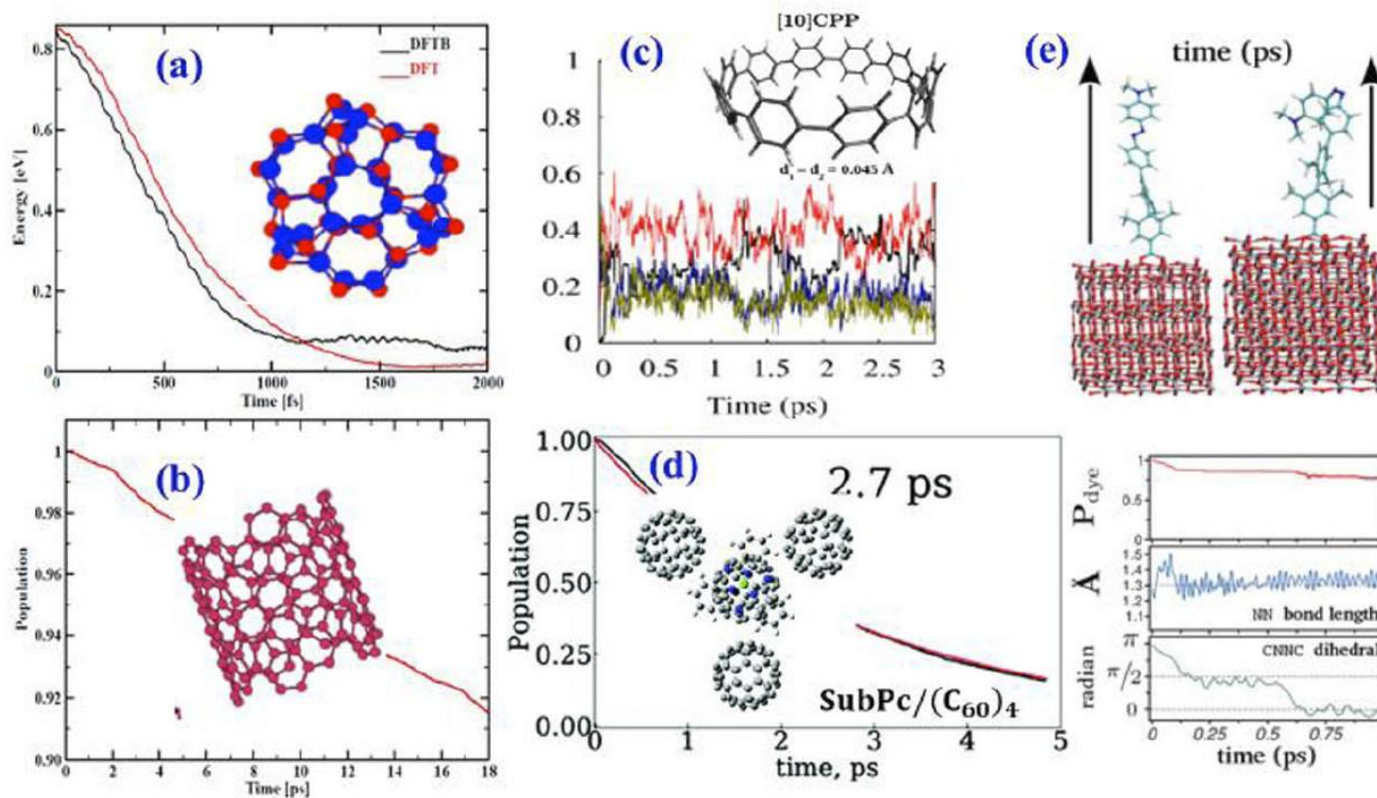


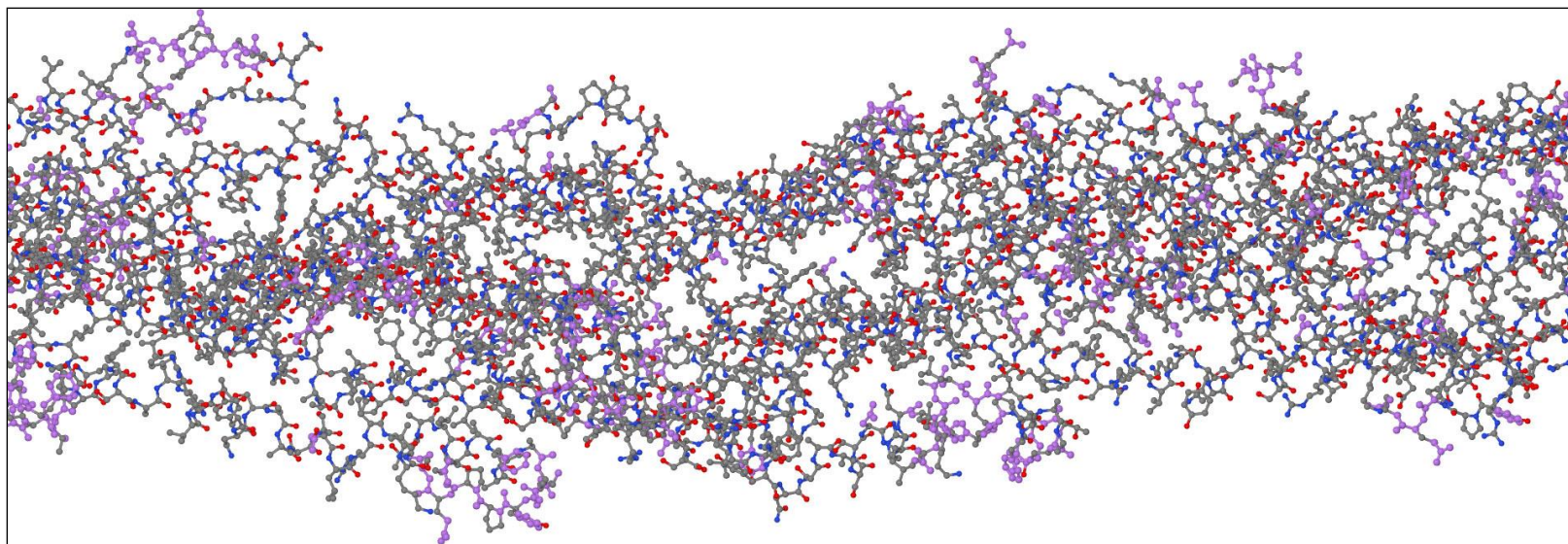
Figure 3. Examples of NA-MD methods for large systems that use DFTB, semiempirical, or semiempirical/molecular mechanics approaches. (a) and (b) DFTB+ is used with NBRA-based NA-MD (Pyxaid) to study the excited states relaxation dynamics in cadmium selenide nanocrystals (a) and carbon nanotubes (b). Adapted from [97], with permissions; Copyright (2016) American Chemical Society; (c) The LC-TD-DFTB approach combined with the general TSH method (Newton-X) enabled modeling the excited states dynamics of CPP. Adapted from [120], with permissions; Copyright (2017) American Chemical Society; (d) Combination of the semiempirical methods available in the GAMESS program with NBRA-based TSH (Libra) enabled studying charge transfer in extended molecular models of organic heterojunctions. Adapted from [133]. CC BY 3.0; (e) combination of EHT with molecular mechanics enabled TSH calculations with electron-nuclear back-reaction, which enabled modeling the photoinduced isomerization of azobenzene derivatives on semiconductor surfaces. Adapted from [135], with permissions; Copyright (2019) American Chemical Society.

DFTB/semiempircs is currently the only approach suitable for NAMD of materials/molecules

Usage 3: Large biomolecular system

Example:

Is there a conductive pathway through π -conjugated system?



MOPAC MOZYME PM7 calculations, 17000 atoms in PBC:
Localization of all occupied MOs up to -11 eV is shown by
violet color – there is no efficient conduction pathway

Adv Mater 27, 1908 (2015)

Historical example...

Role of sp^3 carbon and 7-membered rings in fullerene annealing and fragmentation

Robert L. Murry, Douglas L. Strout,
Gregory K. Odom & Gustavo E. Scuseria*

NATURE · VOL 366 · 16 DECEMBER 1993

Purpose: explore computationally energetics of intermediate species appearing during fullerene fragmentation and annealing, i.e. what happen after laser light breaks C-C bond(s) and how then molecule heals.

Methods used: MNDO (semiempirics), SCF (ab initio), BLYP, LDA (DFT)

Notably, at that time, geometry optimizations of such large molecules were only possible at semiempirical level!

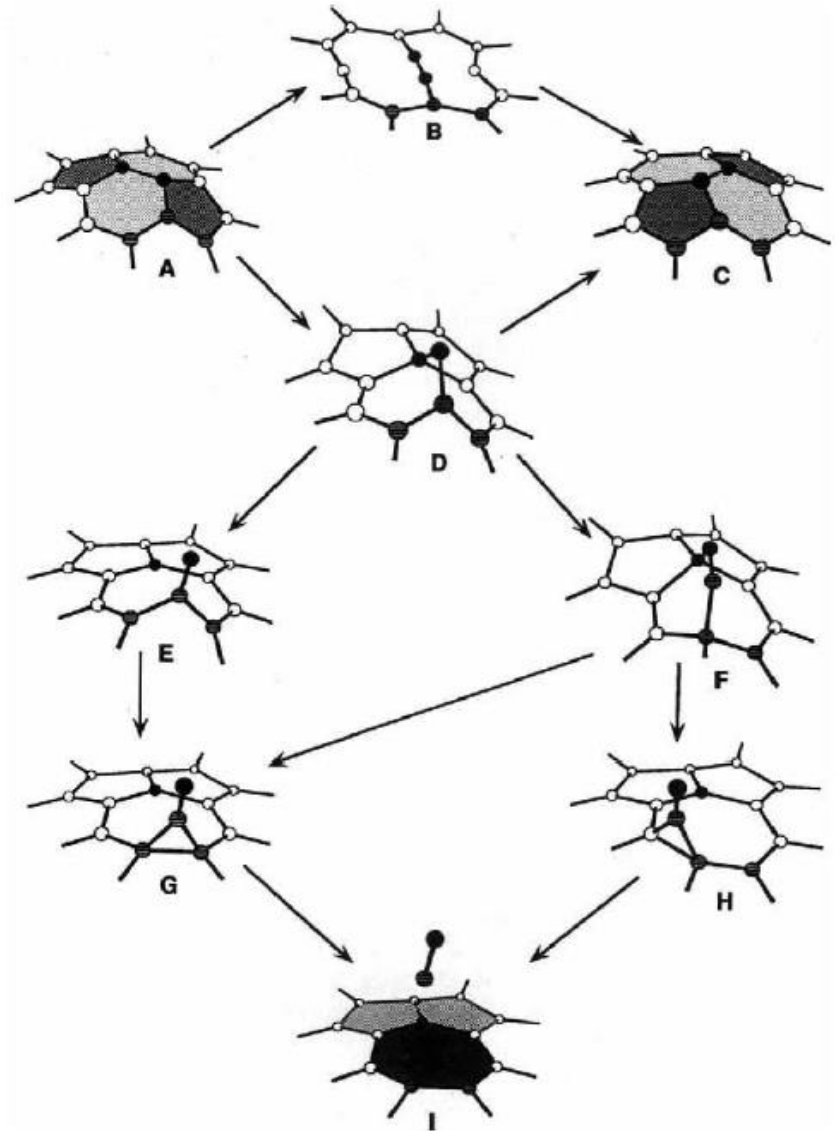


FIG. 1 The Stone–Wales rearrangement and its role in annealing and fragmentation. Atoms and polygons are shaded for ease in following

... Historical example continued...

Role of sp^3 carbon and 7-membered rings in fullerene annealing and fragmentation

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Calculations demonstrate that 'in plane' structure re-arrangements is 'more expensive' energetically, compared to the 'out-of-plane' transitions involving sp^3 configurations

TABLE 1 Energetics of Stone–Wales annealing rearrangement for fullerene model systems

		Barriers (eV)			
		Minimum*		Extended†	
Method	Basis set	In-plane	sp^3 intermediate	In-plane	sp^3 intermediate
MNDO		8.6	5.9	8.2	5.9
SCF	2s1p	11.3	5.5	11.6	7.0
SCF	4s2p	9.6	7.8	9.6	6.3
LDA	4s2p	8.7	6.4	9.3	7.4
BLYP	4s2p	8.4	6.4	8.9	7.1
SCF	4s2p1d	9.5	7.1	9.5	6.1
LDA	4s2p1d	8.1	6.1	8.7	7.1
BLYP	4s2p1d	8.0	6.1	8.4	6.9

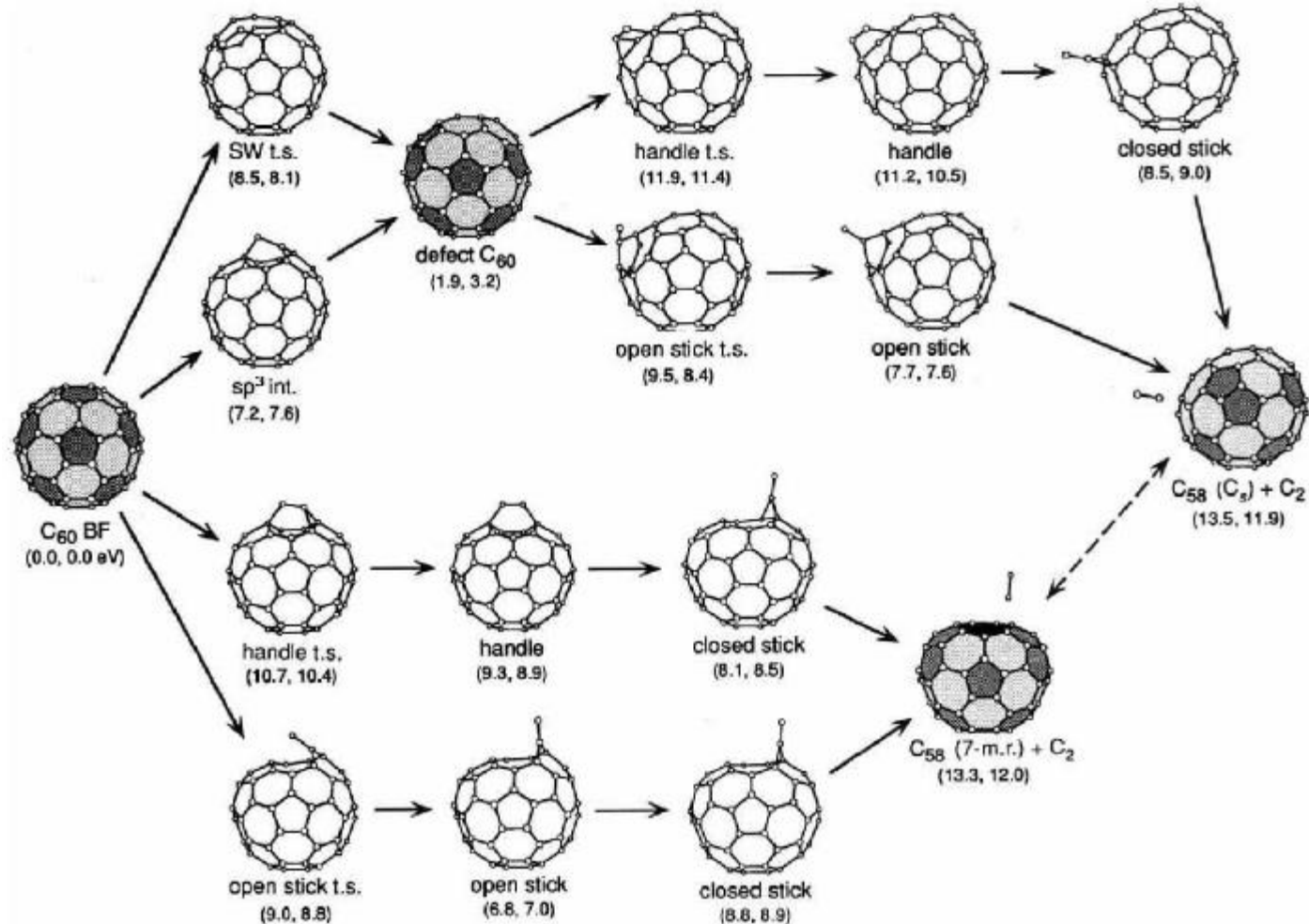
... Historical example continued

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Calculated map of fragmentation and annealing pathways after laser photodamage into stable structures.



Discussion

1. Why all 3c/4c integrals can be neglected? Which 2c integrals can be neglected and which cannot?

$$W_{ikjl} = \langle \varphi_i(x)\varphi_j(y) | W(x, y) | \varphi_k(x)\varphi_l(y) \rangle$$

2. Why for dynamic correlations we prefer DFTB methods and for static correlations we use semiempirical methods?
3. Why we cannot use simple tight binding for biopolymers?
4. Why we cannot use simple tight binding for nonadiabatic molecular dynamics?