Electronic structure calculations and applications

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Electronic Structure (often called Quantum Chemistry) calculations use quantum mechanics to determine the wavefunctions of the electrons in molecules.

With this infomration, one can determine:

1. Structure of the molecule (bond lengths, angles)
2. Electronic energy (bond energies, enthalpies of formation, etc)
3. Spectra (electronic, vibrational, rotational, etc)
4. Electrical properties (dipole moment, polarizability)
5. Molecular orbitals and derived properties such as effective charges, bond orders.
6. Barriers to reaction and other rate properties.
7. Mechanical and transport properties of materials

References:

There are many undergraduate and beginning graduate texts which describe the elements of quantum mechanics as is relevant to molecular electronic structure. Some of my favorites are:

D. A. McQuarrie, Quantum Chemistry, University Science Books, Mill Valley, CA 1983.
C. E. Dykstra, Introduction to Quantum Chemistry, Prentice Hall, Englewood Cliffs, NJ, 1994.
P. W. Atkins and R. S. Friedman, Molecular Quantum Mechanics, 3rd ed, Oxford, New york, 1997.
F. L. Pilar, Elementary Quantum Chemistry, 2nd ed., McGraw-Hill, New York, 1990
M. A. Ratner and G. C. Schatz, Introduction to Quantum Mechanics in Chemistry, Prentice Hall, Englewood Cliffs, 2001.

Quick Primer on Quantum Mechanics as applied to electrons in atoms and molecules

In quantum mechanics, the primary goal is to determine the wave function $\Psi(x,y,z)$. This depends on electron coordinates x,y,z (say for one electron) and it determines the probability density for finding the electron at any position via:

$|\psi(x,y,z)|^2$ = probability density for finding electron at x,y,z

The wavefunction is obtained by solving the Schrödinger equation (1926):

$$H\Psi = E\Psi$$

where H = Hamiltonian operator (described on next slide) and E is the energy.

Hydrogen Atom

Let’s consider an electron of mass m and charge -e bound to a proton (which we take to have infinite mass). The Hamiltonian of the electron describes two effects: the kinetic energy of the electron, and the Coulomb attraction between the electron and the nucleus. This is given by:

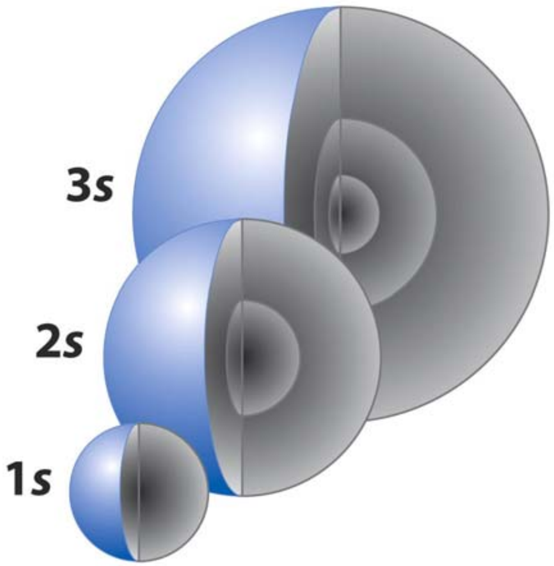
$$H = T + V = \frac{-\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

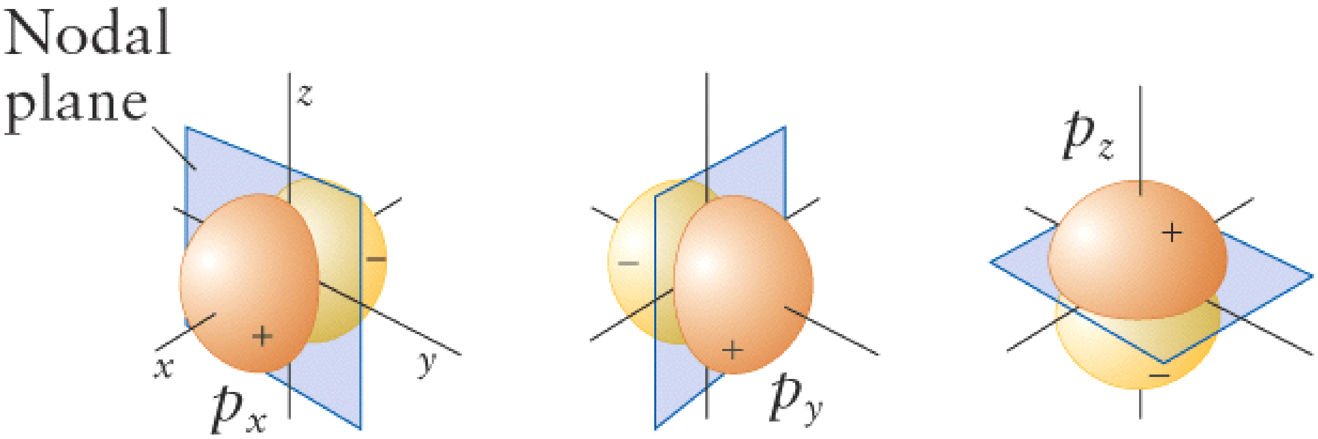
Given this Hamiltonian, it is possible to solve the Schrödinger equation exact by assuming that the wavefunction has the form:

$$\psi(r,\theta,\phi) = R(r)Y_{\ell m}(\theta,\phi)$$

Here R is the radial function (tells you about the probability of finding the electron as a function of the distance from the nucleus) $Y_{\ell m}$ is called a spherical harmonic, and it tells you about the angular dependence of the wavefunction.

This leads to the familiar s, p, d, etc orbitals of the hydrogen atom



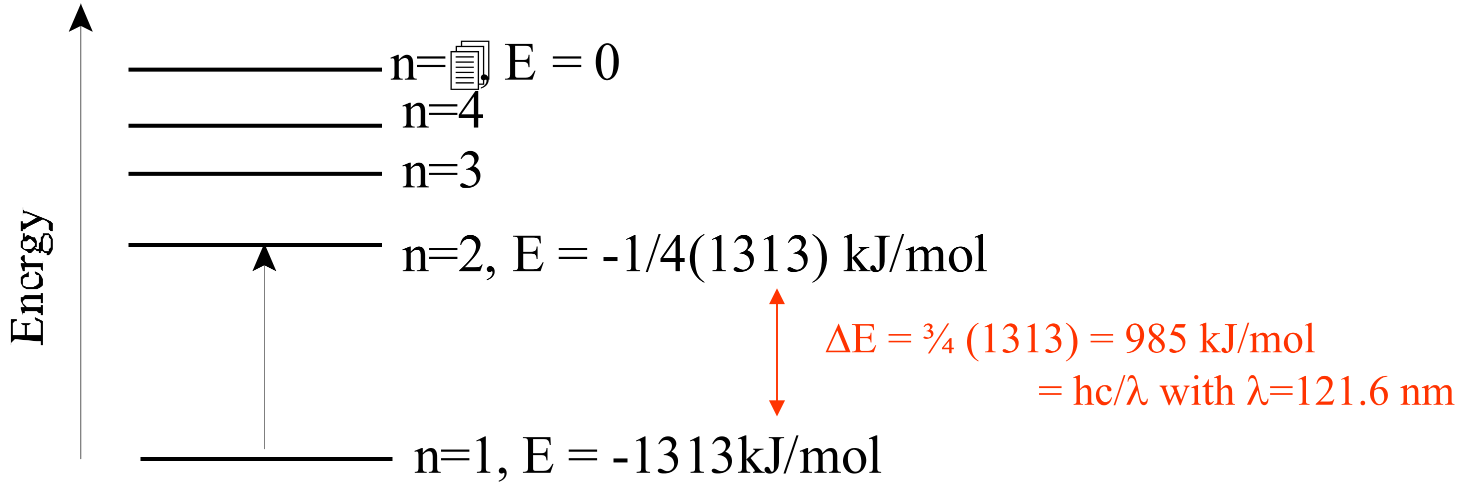


The Schrödinger equation also tells us the energy levels of hydrogen atom:

$$E_n = -\frac{hR}{n^2}$$

n = 1,2,...,4 is called the "principle" quantum number

hR = 1313 kJ/mol = 13.6 eV.



Energy

n=🗐, E = 0

n=4

n=3

n=2, E = -1/4(1313) kJ/mol

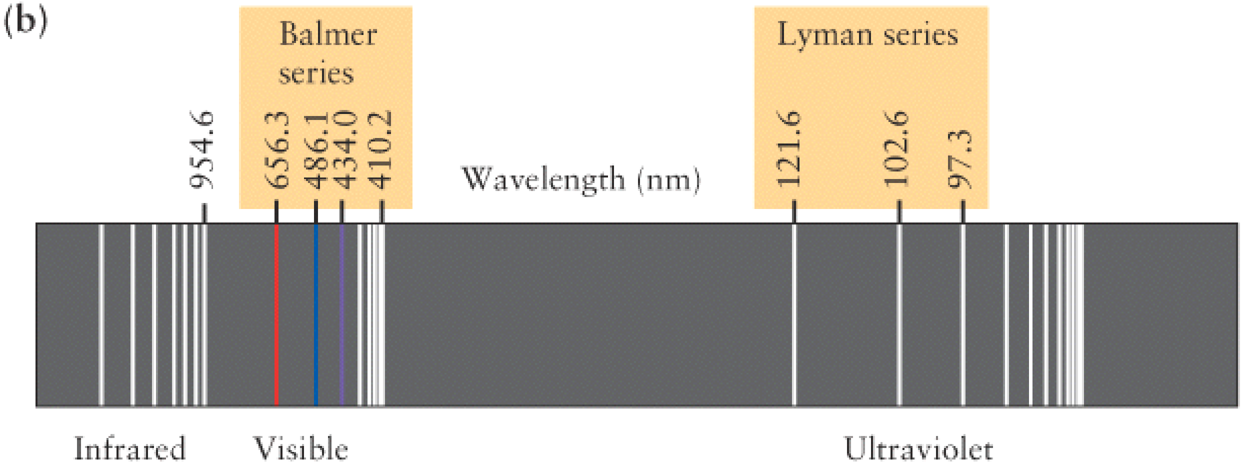
ΔE = ¾ (1313) = 985 kJ/mol
= hc/λ with λ=121.6 nm

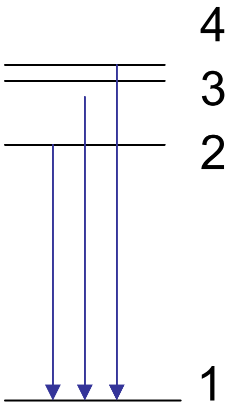
n=1, E = -1313kJ/mol

Once we have the energy levels, we can describe the electronic spectrum of the hydrogen atom

$$\frac{1}{\lambda}=\frac{v}{c}=\frac{E_{n'}-E_{n''}}{hc}=R_H\left[\left(\frac{1}{n''}\right)^2-\left(\frac{1}{n'}\right)^2\right]$$

R_H = 109737.31 cm^{-1} = 13.605698 eV is known as the *Rydberg constant.*





n’=4,5,… → n”=3

n’=3,4,… → n”=2

n’=2,3,… → n”=1

He atom: Can one write a wavefunction as a product of two orbitals:

$$\psi_{\mathrm{He}} = \phi_{1s}(1)\phi_{1s}(2)$$

Pauli Principle: for electrons, the wavefunction, including spin, must be antisymmetric with respect to interchange of any two electrons.

Electron Spin States:

$$\alpha = \left|\frac{1}{2}\,\frac{1}{2}\right\rangle \quad \uparrow \qquad\qquad \beta = \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle \quad \downarrow$$

Including for spin, the $1s^2$ state of He is:

$$\psi_{gr} = \phi_{1s}(1)\phi_{1s}(2)\frac{(\alpha_1\beta_2 - \beta_1\alpha_2)}{\sqrt{2}}$$

Slater determinant form of wavefunction:

$$\psi_{gr} = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_{1s}(1)\alpha_1 & \phi_{1s}(1)\beta_1 \\ \phi_{1s}(2)\alpha_2 & \phi_{1s}(2)\beta_2 \end{vmatrix}$$

$$\begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = -2$$

$$\begin{vmatrix} 3 & 4 \\ 1 & 2 \end{vmatrix} = +2$$

Slater determinants give us a general prescription for writing the wavefunction of any atom or molecule. Thus the wavefunction of the Be atom is:

$$\psi(Be)=\left(\frac{1}{4!}\right)^{1/2}\begin{vmatrix} \phi_{1s}(1)\alpha_1 & \phi_{1s}(1)\beta_1 & \phi_{2s}(1)\alpha_1 & \phi_{2s}(1)\beta_1 \\ \phi_{1s}(2)\alpha_2 & \phi_{1s}(2)\beta_2 & \cdots & \cdots \\ \phi_{1s}(3)\alpha_3 & \phi_{1s}(3)\beta_3 & \cdots & \cdots \\ \phi_{1s}(4)\alpha_4 & \phi_{1s}(4)\beta_4 & \cdots & \phi_{2s}(4)\beta_4 \end{vmatrix}$$

Electronic structure of molecules

The simplest molecule is H_2^+:

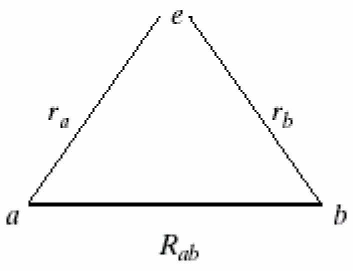


Figure 10.1 Coordinate definitions for H_2^+ molecule.

In this case, the complete Hamiltonian including both nuclei and electrons has the form:

$$\mathrm{H} = \mathrm{T}_\mathrm{n} + \mathrm{T}_\mathrm{e} + \mathrm{V}_\mathrm{en} + \mathrm{V}_\mathrm{nn}$$

Solving the Schrödinger equation with this Hamiltonian is really hard, however since the electrons are so much lighter than the nuclei, it is possible to invoke what is called the **Born-Oppenheimer** approximation, wherein the wavefunction is written as a product:

$$\Psi(\mathrm{r},\ \mathrm{R}) = \underbrace{\psi(\mathrm{r};\ \mathrm{R})}_{\text{electronic}}\underbrace{\chi(\mathrm{R})}_{\text{nuclear}}$$

This leads to two Schrödinger equations to solve, one for the electrons (with the nuclei fixed) and one for the nuclei.

Electronic Schrödinger equation:

$$(T_e + V_{en})\psi = E_{e\ell}\psi$$

Nuclear Schrödinger equation:

$$(T_n + V_{nn} + E_{e\ell})\chi = E\chi$$

In what follows, we'll mostly worry about the electronic Schrödinger equation, but occasionally we will examine the **potential energy surface** $V=V_{nn}+E_{el}$ as this tells us how the nuclei move.

Solving electronic Schrödinger equation: We assume that the molecular orbitals (wavefunctions) are obtained from a linear combination of atomic orbitals (LCAO)

$$\psi = C_a 1s_a + C_b 1s_b$$

If this solution is substituted into the Schrödinger equation, and the coefficients C_a and C_b are optimized, we obtain the following secular equation to determine the energy.

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - E \end{vmatrix} = 0$$

$$H_{aa} = \langle 1s_a | H_{e\ell} | 1s_a \rangle$$

$$H_{ab} = \langle 1s_b | H_{e\ell} | 1s_b \rangle$$

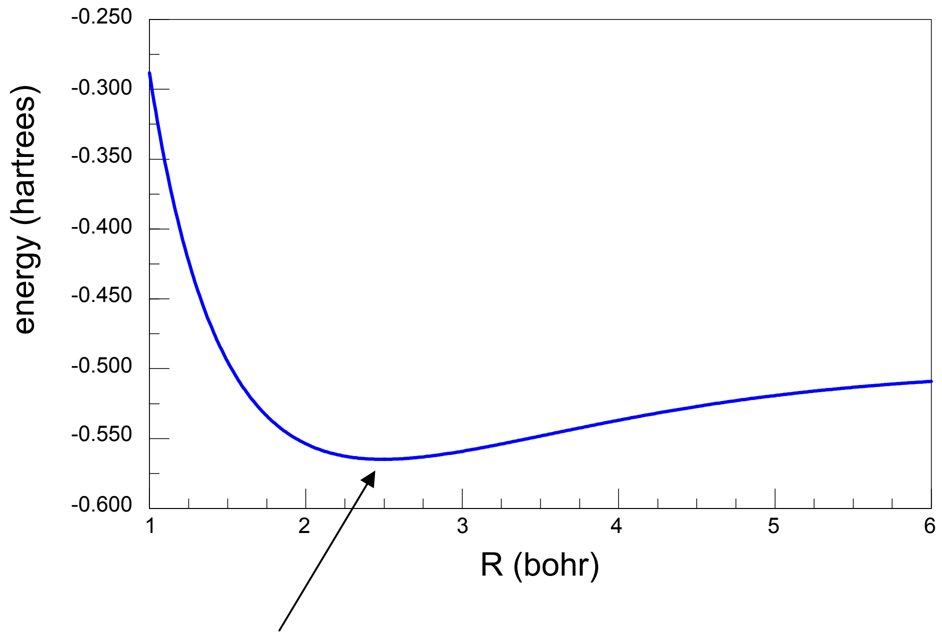
Hamiltonian matrix

$$S_{ab} = \langle 1s_a | 1s_b \rangle$$

Overlap matrix

If this equation is now solved, we obtain the following expression for the ground state H_2^+ energy function:

$$E_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}}$$



R_e =1.32Å (1.066Å exact)
D_e=1.76 eV (2.79 eV exact)

The molecular orbital wavefunctions have the following form:

$$\psi_+ = \sigma_g 1s = N_+(1s_A + 1s_B)$$

$$\psi_- = \sigma_u 1s = N_-(1s_A - 1s_B)$$

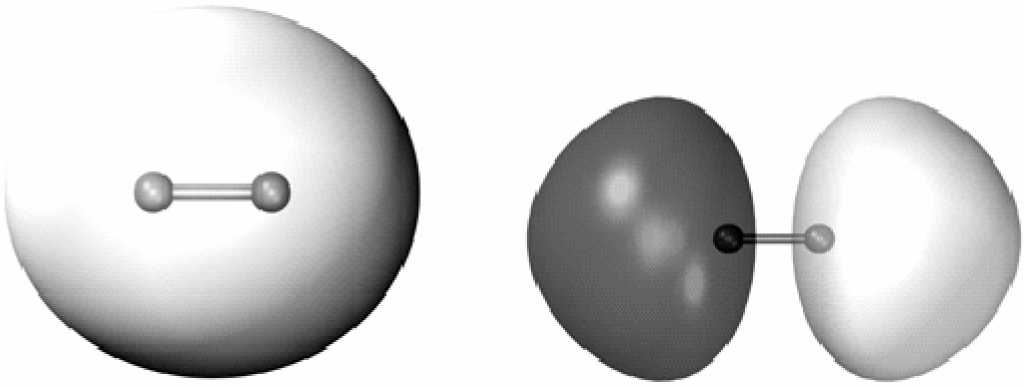


Figure 10.4 Three-dimensional contour plots of ψ_+ and ψ_-. (These are actually the true σ_g 1*s* and σ_u 1*s* orbitals of H_2^+.) The position of the nuclei is indicated using two filled black circles connected by a black line.

Molecular Electronic Structure Calculations

With this introduction, we are now ready to describe electronic structure calculations in a general sense.

Our goal is to solve the Schrödinger equation for the energy of the electrons and the wavefunction, for fixed locations of the nuclei (Born Oppenheimer Approximation). The general form of this equation is:

$$H_{el}\Psi = E_{el}\Psi$$

where H_{el} is known as the Hamiltonian operator (the energy operator for the electrons), E_{el} is the electronic energy, and Ψ is the wavefunction (which depends on the coordinates of the electrons). The Hamiltonian operator for a molecule can be written as:

$$\hat{\mathrm{H}}_{e\ell} = \mathrm{T}_{e} + \mathrm{V}_{en} + \mathrm{V}_{ee}$$

where the first term describes the electronic kinetic energy, the second the attraction of the electrons to the nuclei and the third the electron-electron repulsion.

The kinetic energy operator has the form $T = -\frac{\hbar^2}{2m}\nabla^2$ for each electron, just as in the hydrogen atom.

The attractive and repulsive potentials are determined by the Coulomb interactions between the relevant particles. The general form of the Coulomb interaction is $V_{Coulomb}=q_1q_2/r_{12}$, where q_1 and q_2 are the charges of the two interacting particles and r_{12} is the distance between the particles. Electrons have a charge –e, while nuclei are +Ze, where $e=1.6\text{x}10^{-19}$C, so we have:

$$\hat{H}_{e\ell} = \sum_{i=1}^{N}\left\{-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{j>i}\frac{e^2}{r_{ij}}\right\}$$

Often we will use units for which $\hbar$ =m=e=1. These are known as *atomic units*. In this system of units, we have:

$$\hat{H}_{e\ell} = \sum_{i=1}^{N}\left\{-\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{M}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{j>i}\frac{1}{r_{ij}}\right\}$$

We will learn about three kinds of calculations that “solve” the electronic Schrödinger equation in some sense: *ab initio*, semiempirical and density functional theory.

1) In an ***ab initio*** calculation, the Schrödinger equation is solved using the Hamiltonian given previously, by using basis functions to represent the wavefunction. All terms in the energy expression are calculated rigorously.

2) In a ***semiempirical*** calculation, the procedure is the same, but the energy expression is greatly simplified by letting some terms be expressed in terms of empirical expressions rather than calculated.

3) In a ***density functional theory*** calculation, the energy of the electrons is reexpessed in terms of the electron density rather than the wavefunction, and the density is obtained by solving a Schrodinger-like equation for each electron that includes for interactions with the other electrons.

Ab initio calculations

To solve the Schrödinger equation, we write the many-electron wavefunction in an approximate way, as a product of wavefunctions for each electron. The wavefunctions for the individual electrons are called molecular orbitals, so if we write the total wavefunction as a product of orbitals, this means that each electron “does its own thing”, seeing only the average repulsion due to the other electrons. This theory is called Hartree-Fock theory.

We have to obey the Pauli principle, so the product of orbitals needs to be made antisymmetric with respect to interchange of electrons. To achieve this, we use a Slater determinant (see below), as this is a mathematical device that permutes the electrons among the orbitals with appropriate signs so that the wavefunction is antisymmetric with respect to exchange of any two electrons. The resulting theory can be developed with the restriction than the up and down-spin orbitals be the same (restricted Hartree-Fock) or without this restriction (unrestricted HF).

$$\psi = \frac{1}{\sqrt{N!}} \left| \begin{array}{llll} \phi_1(1)\alpha_1 & \phi_1(1)\beta_1 & \phi_2(1)\alpha_1 & \phi_2(1)\beta_1 \ldots \\ \phi_1(2)\alpha_2 & \phi_1(2)\beta_2 \cdots & & \\ \quad \cdots & & & \\ \quad \cdots & & & \\ \phi_1(N)\alpha_N & \phi_1(N)\beta_N \ldots & & \end{array} \right|$$

Determining the orbitals

If we assume that the wavefunction Ψ is a Slater determinant, then the best possible orbitals in that determinant are obtained by solving the Hartree-Fock equations:

$$\hat{f}_k \phi_k = \varepsilon_k \phi_k$$

where f is called the Fock operator, Φ is the orbital and ε is the orbital energy. These equations are a lot like Schrödinger equations for each electron, and the “Hamiltonian” is sort of like a Hamiltonian for each electron. Thus we have:

$$\hat{f}_k = -\frac{1}{2}\nabla_k^2 - \sum_{\alpha}\frac{Z_\alpha}{r_{k\alpha}} + \sum_j \left(2J_j(k) - K_j(k)\right)$$

where the first term describes kinetic energy, the second the attraction to the nuclear, and the remaining two describe Coulomb and Exchange interactions.

LCAO-MO method

To solve the HF equations, we expand each molecular orbital in terms of a linear combination of atomic orbitals. For example, for the H_2^+ molecule, the ground state orbital is expressed as a sum of 1s orbitals on each atom, i.e., $\phi = c_a 1s_a + c_b 1s_b$, where the “a” and “b” labels refer to the two nuclei, and c_a and c_b are coefficients for each orbital that we would optimize to give the best possible energy. More generally, we would write:

$$\phi_k = \sum_v c_{kv} b_v$$

where “b_v” stands for the vth atomic orbital basis function and c_{kv} are coefficients that determine the contribution of the vth basis function to the kth molecular orbital. We will talk about basis functions later, but for now we note that these would be 1s, 2p, 3d and other orbitals that are centered on the atoms.

The coefficients c_{kv} are optimized to give the best possible solution. Using variational theory, one can show that this optimization process is the one that gives the lowest molecular orbital energies ε_k.

Secular equation

We won’t go through the details, but variational theory leads to the following equation (known as the secular equation) to determine the molecular orbital energies ε:

$$\left|\mathbf{f} - \varepsilon\mathbf{S}\right| = 0$$

This equation is called the secular equation, and it says that the determinant of the difference between two matrices **f** and ε**s** must equal zero. The f matrix is obtained from the Fock operator:

$$f_{\mu\nu} = \left\langle b_{\mu} \middle| \hat{f} \middle| b_{\nu} \right\rangle$$

while the s matrix involves the overlaps of the atomic orbital basis functions:

$$S_{\mu\nu} = \left\langle b_{\mu} \middle| b_{\nu} \right\rangle$$

Solving the Hartree-Fock equations and obtaining molecular properties

The secular equation is used to determine the orbital coefficients c_{kv}, and therefore the molecular orbitals. In Hartree-Fock theory, this is only the first step of an iteration procedure, as the Coulomb and Exchange terms in the Fock operator depend on the orbitals. To continue, one uses the newly obtained orbitals to construct a new Fock operator, then solves the HF equations to generate energies ε and additional estimates of the orbitals. After iterating this process, one eventually obtains orbitals that are invariant to further iteration. Once this is done, the total energy E_{el} is calculated.

Much of the technology for HF calculations (and much more) was developed by John Pople, who used to be a professor at Northwestern. Pople received the Nobel Prize for this work in 1998.

Molecular Orbitals and Hartree-Fock Energies

As an example of the application of HF theory, the next two slides show the molecular orbitals of the water molecule. This molecule has 10 electrons, so there are 5 occupied molecular orbitals in the ground state. The first slide (Table 1) shows that these five orbitals have energies that vary from -20.541 to -0.50066 hartrees (1 hartree = 27.211 eV = 627.51 kcal/mol). The matrix in this slide gives the orbital coefficients c_{kv}, showing how each orbital is decomposed into atomic orbitals on each atom.

The second slide (Figure 1) shows pictures of the orbitals. This indicates that the orbital with energy -20.541 (labeled “1”) is primarily localized on the oxygen atom, and it has no nodal surfaces (surfaces where the wavefunction goes to zero). We can consider that this orbital is a 1s function associated with the oxygen atom. Orbital “2” is mostly oxygen 2s, while orbitals 3 and 4 describe bonding between the O and H’s. Orbital 5, the highest occupied molecular orbital (HOMO) is mostly a lone pair associated with an oxygen 2p that is perpendicular to the plane of the molecule.

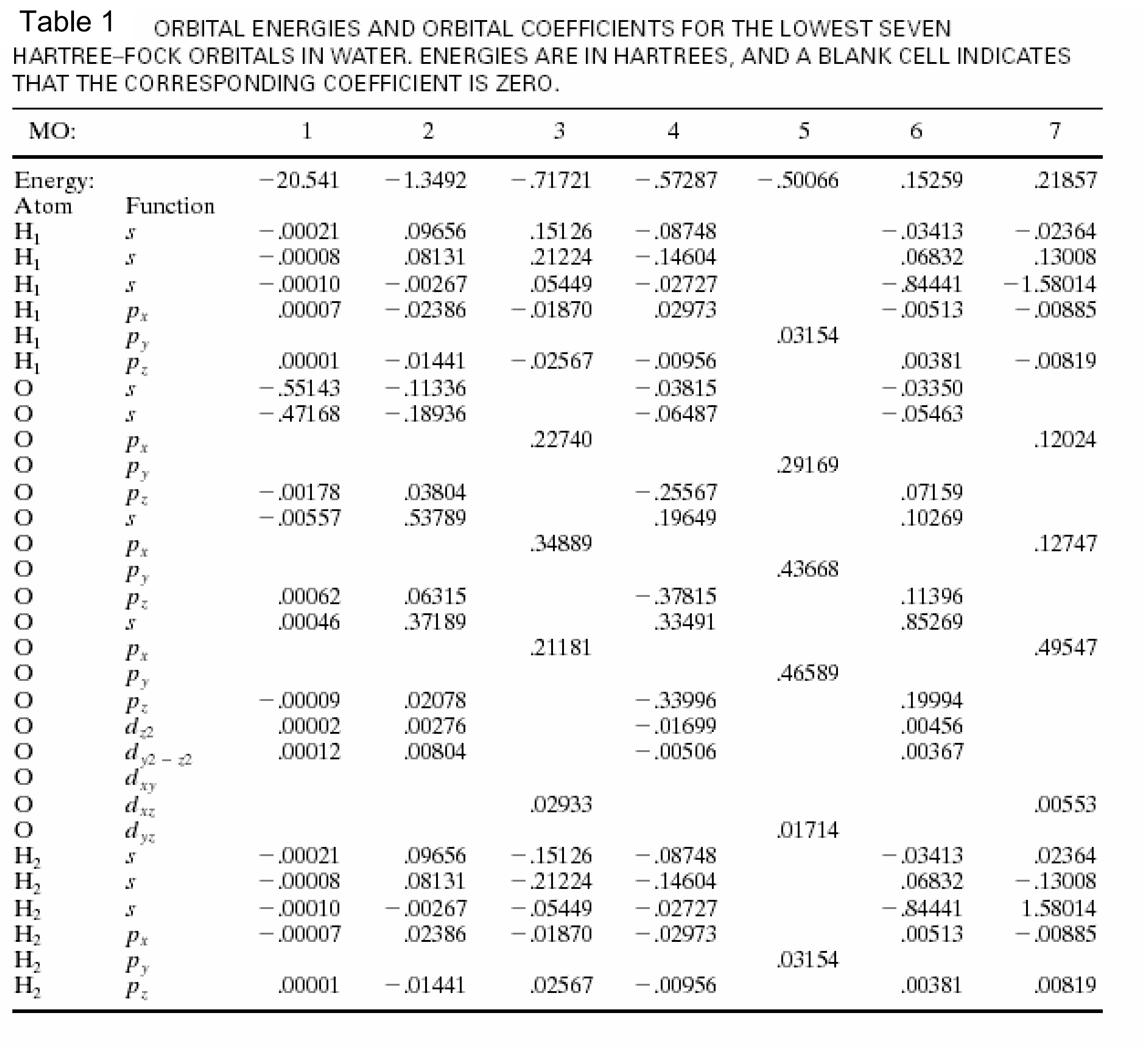
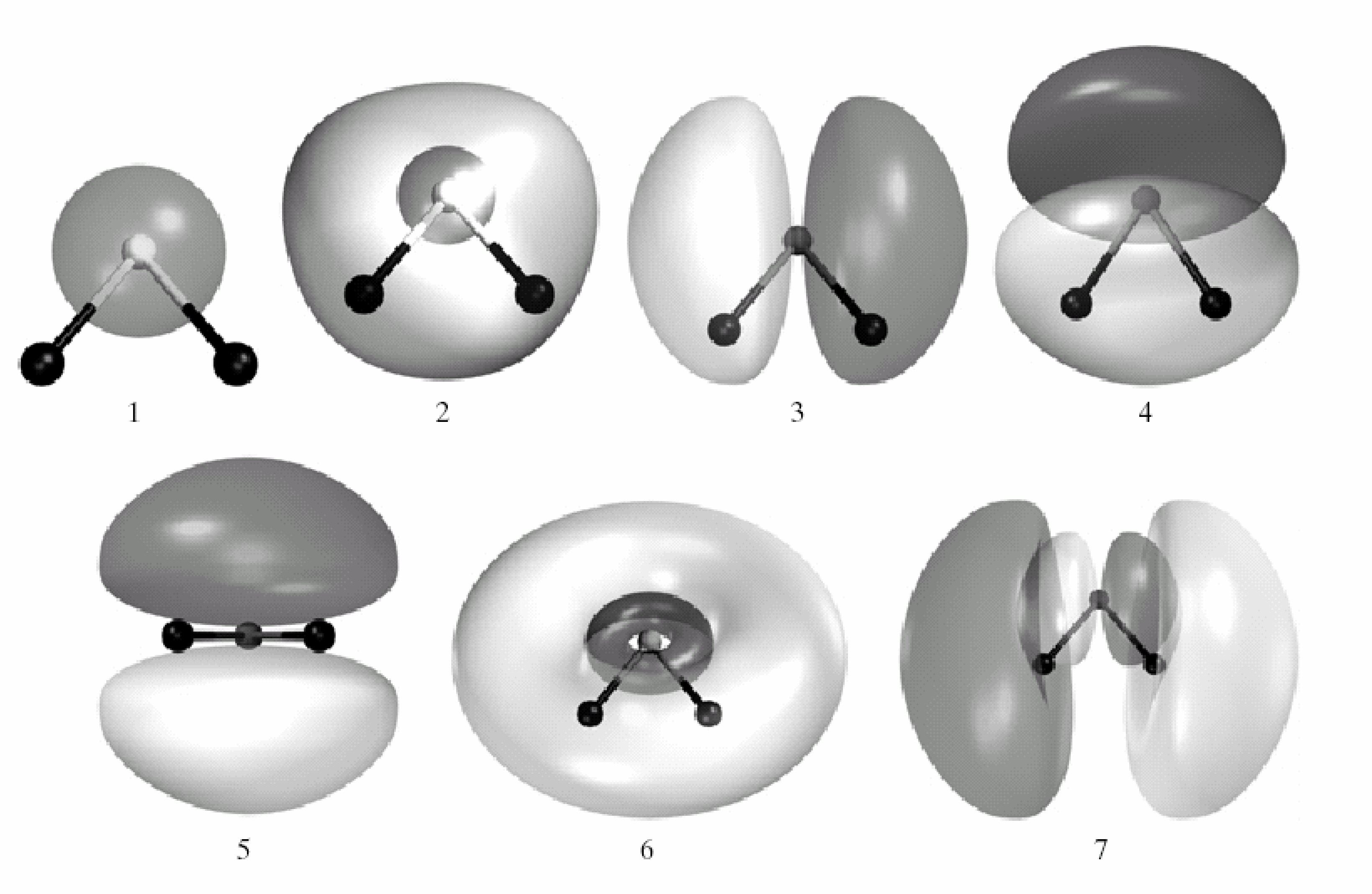


Table 1 ORBITAL ENERGIES AND ORBITAL COEFFICIENTS FOR THE LOWEST SEVEN HARTREE–FOCK ORBITALS IN WATER. ENERGIES ARE IN HARTREES, AND A BLANK CELL INDICATES THAT THE CORRESPONDING COEFFICIENT IS ZERO.

MO:		1	2	3	4	5	6	7
Energy:		−20.541	−1.3492	−.71721	−.57287	−.50066	.15259	.21857
Atom	Function							
H_1	s	−.00021	.09656	.15126	−.08748		−.03413	−.02364
H_1	s	−.00008	.08131	.21224	−.14604		.06832	.13008
H_1	s	−.00010	−.00267	.05449	−.02727		−.84441	−1.58014
H_1	p_x	.00007	−.02386	−.01870	.02973		−.00513	−.00885
H_1	p_y					.03154		
H_1	p_z	.00001	−.01441	−.02567	−.00956		.00381	−.00819
O	s	−.55143	−.11336		−.03815		−.03350	
O	s	−.47168	−.18936		−.06487		−.05463	
O	p_x			.22740				.12024
O	p_y					.29169		
O	p_z	−.00178	.03804		−.25567		.07159	
O	s	−.00557	.53789		.19649		.10269	
O	p_x			.34889				.12747
O	p_y					.43668		
O	p_z	.00062	.06315		−.37815		.11396	
O	s	.00046	.37189		.33491		.85269	
O	p_x			.21181				.49547
O	p_y					.46589		
O	p_z	−.00009	.02078		−.33996		.19994	
O	d_{z2}	.00002	.00276		−.01699		.00456	
O	d_{y2-z2}	.00012	.00804		−.00506		.00367	
O	d_{xy}							
O	d_{xz}			.02933				.00553
O	d_{yz}					.01714		
H_2	s	−.00021	.09656	−.15126	−.08748		−.03413	.02364
H_2	s	−.00008	.08131	−.21224	−.14604		.06832	−.13008
H_2	s	−.00010	−.00267	−.05449	−.02727		−.84441	1.58014
H_2	p_x	−.00007	.02386	−.01870	−.02973		.00513	−.00885
H_2	p_y					.03154		
H_2	p_z	.00001	−.01441	.02567	−.00956		.00381	.00819

Figure 1: Molecular orbitals for H_2O



Atomic Orbital Basis Functions

To solve the Hartree-Fock equations, the orbitals Φ are expanded in a basis set of atomic basis functions. Instead of using hydrogen atom functions for this expansion, the codes commonly use simpler functions. Long ago, Slater developed orbitals (known as STO's, or Slater type orbitals) that have the form:

$$b = Ae^{-\zeta r} r^{n^*-1} Y_{\ell m}(\theta,\phi)$$

These are like hydrogen atom functions, but with a simplified dependence on the radial coordinate r that consists of an exponential times a power in r. Although the Slater orbitals are quite effective, integrals involving the Fock operator are difficult. An alternative that circumvents this are Gaussian functions of the radial coordinate multiplied by spherical harmonics for the angles around each atom:

$$g = x^a y^b z^c e^{-\alpha r^2} Y_{\ell m}(\theta,\phi)$$

Individual gaussians don't look like hydrogen atom orbitals, but this can be fixed by summing many gaussians:

$$b_\mu = \sum_p k_{\mu p} g_p$$

This gives us basis functions like STO-3G in which three gaussians are summed to give functions that look a lot like the hydrogen atom orbitals. The more gaussians the better, so STO-6G (i.e., adding 6 gaussian functions) is an improvement over STO-3G.

Additional types of Gaussian-orbital basis functions

Split Valence Basis

To improve accuracy, it is helpful to use multiple atomic basis functions for each electron shell. Thus 6-31G is a split-valence basis in which there are two independent basis functions for each valence electron.

Polarization Functions

Additional can be achieved with the use of polarization functions, which are functions with one unit of angular momentum higher than would normally be found for the valence electrons. These functions allow the orbitals to distort as a result of bond formation. A common basis function that includes polarization functions is called 6-31G**.

Diffuse Functions

For some problems it is important to include Gaussians with small exponents to describe the “tail” of the wavefunction. An example of a commonly used basis function in this category is 6-31+G.

Beyond Hartree-Fock:

The Hartree-Fock equations are Schrödinger-like equations but they apply to one electron that interacts with the average potential due to all the other electrons. The Fock operator contains the kinetic energy of this electron, the attractive Coulomb interaction with the nuclei, the average repulsion with the other electrons and an attractive interaction with the other electrons that arises from the Pauli principle (the exchange interaction).

What is left out in HF theory is correlation between the electrons. There are many approaches for adding this back in, of which the most commonly used is called MP2 (second order Moller-Plesset) theory. Even better theories are coupled cluster theory and multireference self consistent field theory. By systematically increasing the sophistication of these methods, it is possible to approach the exact solution to the Schrödinger equation. This is a key advantage of ab initio methods that is not available with other theories. However ab initio methods beyond MP2 are generally not feasible, so other methods, such as density functional theory, are more popular.

Semiempirical Molecular Orbital Theory

In semiempirical methods (mostly invented by John Pople), one uses a Slater determinant of orbitals as before, and this generates a secular equation containing overlap and Fock matrices, however the elements in these matrices are approximated in semiempirical methods ,often replacing hard integrals with empirical functions.

There are many kinds of semiempirical methods:

(a) Huckel theory: appropriate to the π electrons in an aromatic hydrocarbon.
(b) Extended Huckel theory: Similar to Huckel, but all electrons are described.
(c) NDO Methods: CNDO and INDO: These methods attempt to mimic Hartree-Fock calculations, but integrals involving Coulomb and Exchange are mostly approximated.
(d) AM1, PM3 are similar to INDO, but integrals are parametrized to match experiment.

Huckel Theory

In Huckel theory, we assume that the σ bonding framework is frozen, and only π bonding is of interest. The wavefunction is expanded in terms of a linear combination of p-π orbitals on all the C, N, O atoms:

$$H\psi = E\psi \qquad \psi = \sum_n c_n \chi_n$$

The secular equation (say for a basis set of two orbitals) has the form.

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{vmatrix} = 0$$

In Huckel-Theory we assume that the overlaps S_{nm} are zero unless n=m, in which case S is unity.

$$H_{nm} = \begin{cases} \alpha_n & \text{for } n = m \\ \beta_{nm} & \text{for atom } n \text{ adjacent to atom } m \\ 0 & \text{otherwise} \end{cases}$$

where α_n and β_{nm} are parameters of the model.

Example of application of Huckel: ethylene $H_2C=CH_2$
Since there are two p-π electrons. the secular equation becomes:

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

The energy levels are:

$$E = \begin{cases} \alpha - \beta \\ \alpha + \beta \end{cases}$$

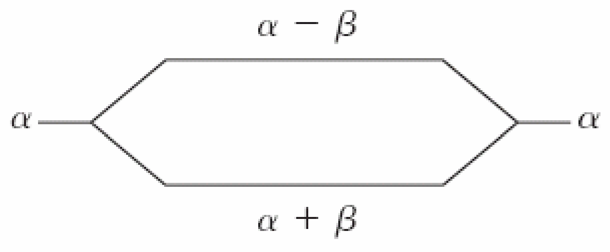


Figure 12.2 Hückel energy levels for ethylene.

Applying the aufbau principle, we would put the two p-pi electrons in the lowest energy level, so that the total energy is:

Total energy = 2α+2β

and the lowest excitation energy is +2|β|. Comparison with experiment can be done by assigning values to α and β.

Extended Huckel

In this approach, one uses all the valence orbitals on the atoms, and then replaces integrals by:

$$H_{nm} = \begin{cases} \alpha_n & \text{for } n = m \\ KS_{nm} \end{cases}$$

where S_{nm} are the calculated overlap integrals between orbitals n and m and K is a parameter.

Semiempirical methods avoid the calculation of expensive integrals, and as a result the computational effort is much less than either HF or DFT. However accuracy is less too.

NDO Methods: A more advanced set of semiempirical theories are called NDO methods, where NDO stands for neglect of differential overlap.

$$\left\langle \mu v \middle| \sigma \lambda \right\rangle = \left\langle b_\mu(1) b_\sigma(2) \middle| \frac{1}{r_{12}} \middle| b_v(1) b_\lambda(2) \right\rangle$$

Pople's most commonly used NDO methods are called CNDO and INDO:

a. CNDO (complete neglect of differential overlap): This is a similar method to extended Huckel, but with two electron integrals negected when μ≠v and σ≠λ. The nonzero integrals were chosen to reproduce the results of accurate HF calculations.

b. INDO (intermediate neglect of differential overlap): Here we include exchange between electrons on the same atom.

In the 1960's and thereafter, Michael Dewar converted INDO into AM1 and PM3, wherein the parameters were redefined to match experimental data.

Density functional theory

Density functional theory (DFT) is another way to do electronic structure calculations that looks and acts a lot like HF theory, but in the end produces higher quality results with the same or less effort. The equations being solved (the Kohn-Sham equations) have the same form as the HF equations but the Fock operator is different, with effects due to electron correlation directly included.

The starting part of this theory is the Hohenberg-Kohn theorem, which states that the electronic energy E of any molecule can always be expressed as a functional of the electron density ρ (i.e., not requiring the wavefunction Ψ). This energy has the form:

$$E = T + V_{\text{nucl}} + V_{\text{rep}} + E_{\text{xc}}$$

where here we have generalized our earlier Hartree-Fock expression to include for the exchange and correlation energy E_{xc}.

To show how this works, here are expressions for the electron-nuclear attraction and the electron-electron repulsion in terms of the density ρ

$$V_{\text{nucl}} = -\sum_{\alpha} \int \frac{Z_{\alpha}\rho(1)}{r_{1\alpha}} d\tau_1$$

$$V_{\text{rep}} = \frac{1}{2} \iint \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2$$

The electron density can be expressed in terms of the occupied molecular orbitals using

$$\rho = \sum_{\text{i(occupied)}} |\phi_{\text{i}}|^2$$

However in H-K theory, one doesn’t need to have wavefunctions, as only the density is needed.

Although it was easy to express the Coulomb attractive and repulsive terms as functionals of the density, however the kinetic energy is a challenge. The exact expression is:

$$\mathrm{T} = -\frac{1}{2}\sum_{\mathrm{i}}\int \phi_{\mathrm{i}}\nabla^{2}\phi_{\mathrm{i}}\,\mathrm{d}\tau$$

The exact expression for T in terms of ρ is not known, however a rough approximation is given by the local density approximation (LDA):

$$T = \frac{3}{10}(3\pi^{2})^{2/3}\int \rho^{5/3}\,d\tau$$

Better expressions are known, but the LDA is good enough to get started.

The last part of the energy expression is the exchange-correlation energy. Again there is no known exact expression, but a local density approximation is:

$$E_{\mathrm{xc}} = -\frac{9}{8}\left(\frac{3}{\pi}\right)^{1/5}\alpha\int \rho(1)^{4/3}\,d\tau_{1}$$

where α is 1 (rigorously) but is usually allowed to vary to improve the quality of the results.

Kohn-Sham Theory

The theory to this point only requires the density matrix. However the absence of an exact expression for the kinetic energy is a serious problem. To circumvent this, we go back to a wave-function based theory for the kinetic energy but stay with density functional expressions for everything else. This leads to a Hartree-Fock-like equation for the orbitals as follows:

$$\mathrm{F}\phi = \varepsilon\phi$$

where the Kohn-Sham operator is:

$$F(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha}\frac{Z_a}{r_{1a}} + \sum_j J_j(1) + V_{\mathrm{xc}}$$

$$V_{\mathrm{xc}} = \frac{\partial E_{\mathrm{xc}}}{\partial \rho}$$

$$\rho = \sum_{\mathrm{i}} \left|\phi_{\mathrm{i}}\right|^2$$

Gradient Corrected DFT:

The theory defined to this point is called LDA, local density functional approximation. This theory is not adequate for most applications, but it is possible to improve it by adding terms to the exchange-correlation functional that depend on gradients of the electron density.

The most commonly used expression is called B3LYP, developed in 1993. This acronym stands for the names of the people who contributed important parts to the energy expression, namely Becke, who developed an expression for the exchange energy, and Lee-Yang-Parr, who developed an expression for the correlation energy. In B3LYP, terms in the exchange and correlation energy expressions were combined using three adjustable parameters (hence the “3") that were optimized so as to give accurate heats of formation for a large number of molecules. Thus B3LYP has empirical components to it (unlike HF), and in many respects it is no accident that it is more accurate.

Summary of Electronic Structure Methods:

Hartree-Fock Theory: ROHF, UHF

Beyond HF (there is no “beyond” for DFT):

- MP2, MP4 – 2nd and 4th order perturbation theory (starting with HF)
- CCSD – Coupled Cluster singles and doubles (starting with HF)
- MCSCF, CASSCF – Multireference SCF, Complete Active Space SCF

Semiempirical Theory

- Huckel
- Extended Huckel
- CNDO, INDO
- PM1, AM1

Density Functional Theory

- LDA
- B3LYP

Properties that can be obtained from Electronic Structure Calculations

So far we have emphasized the calculation of the electronic energy and molecular orbitals. However there are many other properties that can be determined once we have the wavefunction in hand. Here is a brief summary.

1. Potential energy surface ($V_n = E_{el} + V_{nn}$):

Dissoc Energy = $V_n(Q_n^{diss}) - V_n(Q_n^{equil})$

Note: Need to add in vibrational zero point energy to determine ΔE(T=0), and need to calculate partition functions to get ΔE(T). Additional work provides other thermodynamics functions.

2. Wavefunction and orbitals: used to determine electron density

$\Phi_k(q_e; Q_n)$ $\quad\quad$ $\Psi = |\,\Phi_1\,\Phi_2\,\Phi_3\,...|$

3. Electrostatic Moments (dipole moment, etc) and electrostatic potential

Q = charge

$$\mu = \left\langle \Psi \middle| \sum_i e r_i \middle| \Psi \right\rangle = \frac{\partial E_{el}}{\partial F} \qquad q_{kl} = \langle \Psi | \sum_i e r_{ik} r_{il} | \Psi \rangle = \frac{\partial E_{el}}{\partial G}$$

$$V_{elst} = \frac{Q}{R} + \frac{\hat{n}\cdot\mu}{R^2} + \frac{\hat{n}\cdot q\cdot\hat{n}}{R^3} + \cdots$$

4. Gradients, Hessians of the potential energy surface

$$\frac{\partial^m V_n}{\partial Q_n^m}$$

Gradients: $\Rightarrow \frac{\partial V_n}{\partial Q_n} = 0$ at stationary pts

Hessians: $\Rightarrow \frac{\partial^2 V_n}{\partial Q_n \partial Q_{n'}} = H_{nn'}$

Vib frequencies: $\left| \frac{H_{nn'}}{\sqrt{m_n m_{n'}}} - \omega_n^2 I_{nn'} \right| = 0$

5. Polarizabilities

$$\alpha_{ij} = \frac{\partial^2 V_n}{\partial F_i \partial F_j}$$

Hyperpolarizabilities

$$\beta_{ijh} = \frac{\partial^3 V_n}{\partial F_i \partial F_j \partial F_h}$$

6. Magnetic moments, chemical shifts, hyperfine couplings

Effective Charges

There are no unique charges that can be attached to each atom. However there are several definitions that yield useful results in some cases.

1.Atomic charges, bond orders

$$\phi_k = \sum_v C_{kv} b_v$$

Mulliken charges:

$$q_\mu = \sum_i n_i \left|C_{i\mu}\right|^2$$

$$n_{\mu\nu} = \sum_i n_i C_{i\mu} C_{i\nu}$$

Lowdin charges:

$$b'_\mu = \sum_\nu (S^{-1/2})_{\mu\nu} b_\nu$$

$$q_\mu = \sum_i n_i \left|C'_{i\mu}\right|^2$$

2.AIM (Bader) charges: partition the molecule in atoms using the topology of the electron density

3.RESP (restrained electrostatic potential) charges

a. atom centered
b. bond midpoints
c. lone pairs

Calculate E_{el} at several q_N and minimize.

$$\sum_{q_N} \left(V_n(q_N) - V_{ESP}(q_n) \right)^2$$

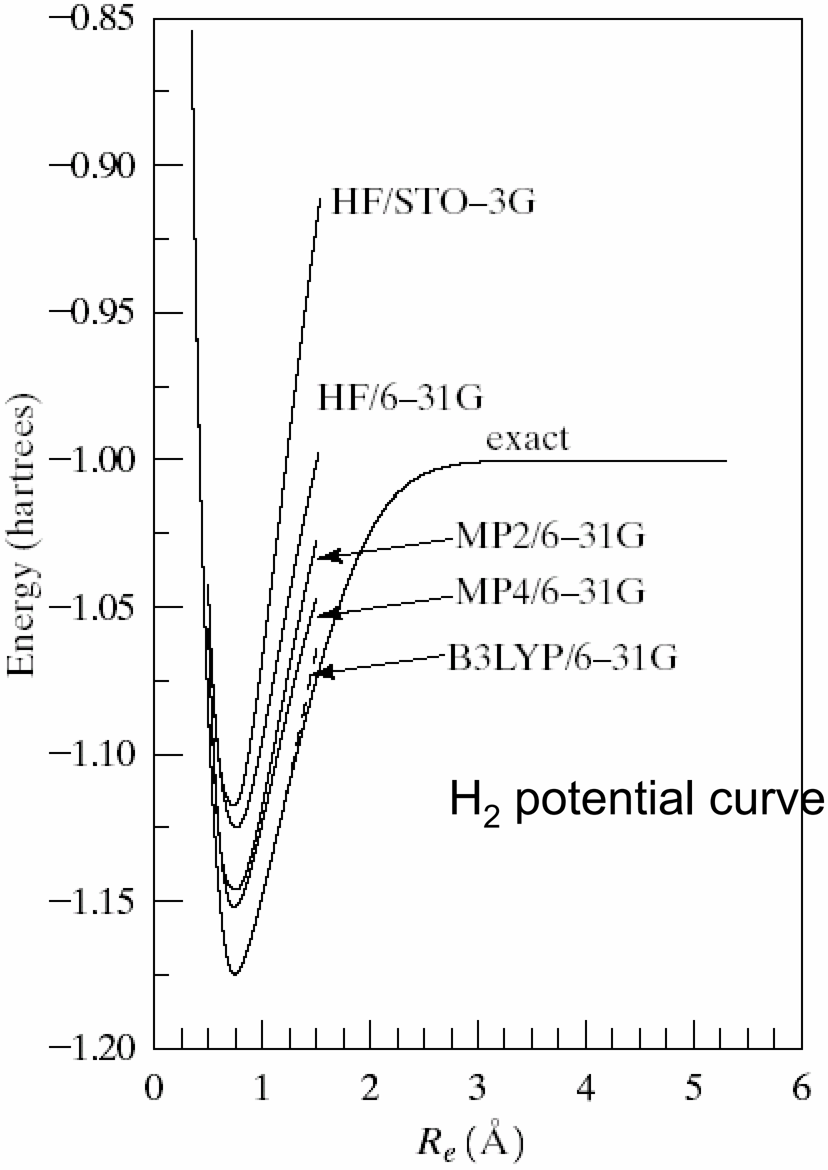
$$V_{ESP} = \sum_{\text{sites } \mathbf{s}} \frac{Q_s}{\left|R_s - q_N\right|}$$

Constraint:

$$Q = \sum_s Q_s$$

$$\mu = \sum_s Q_s \mathit{R}_s$$

Results from electronic structure calculations: potential energy curves, equilibrium geometries, dissociation energies of H_2



H_2 potential curve

Figure 14.1 Potential-energy curves for H_2.

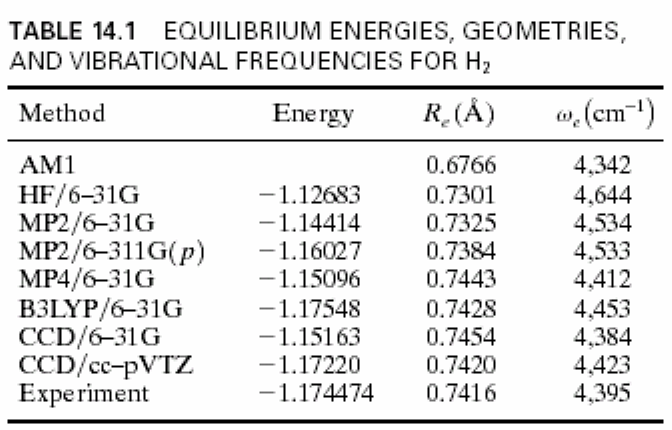


TABLE 14.1 EQUILIBRIUM ENERGIES, GEOMETRIES, AND VIBRATIONAL FREQUENCIES FOR H_2

Method	Energy	R_e (Å)	ω_e (cm^{-1})
AM1		0.6766	4,342
HF/6–31G	−1.12683	0.7301	4,644
MP2/6–31G	−1.14414	0.7325	4,534
MP2/6–311G(p)	−1.16027	0.7384	4,533
MP4/6–31G	−1.15096	0.7443	4,412
B3LYP/6–31G	−1.17548	0.7428	4,453
CCD/6–31G	−1.15163	0.7454	4,384
CCD/cc–pVTZ	−1.17220	0.7420	4,423
Experiment	−1.174474	0.7416	4,395

TABLE 14.2 ENERGY, STRUCTURE AND VIBRATIONAL FREQUENCIES OF H_2O

Method	Energy (E_h)	R_e(Å)	θ (deg)	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})
AM1		0.9612	103.6	3,505	1,884	3,584
HF/STO–3G	−74.96590	0.9895	100.0	4,139	2,170	4,390
HF/6–31G	−75.98536	0.9496	111.6	3,988	1,737	4,146
MP2/6–31G	−76.11318	0.9748	109.3	3,654	1,663	3,830
MP2/6–31G(d,p)	−76.19685	0.9687	104.0	3,775	1,735	3,916
MP4/6–31G	−76.20725	0.9704	103.9	3,739	1,742	3,870
MP4/6–311G(d,p)	−76.27634	0.9590	102.4	3,879	1,680	3,977
B3LYP/6–31G	−76.40895	0.9685	103.6	3,730	1,713	3,851
Experiment	−76.48038[a]	0.9752[a]	104.5[a]	3,833[b]	1,649[b]	3,943[b]

[a] Energy is based on an analysis presented by A. Lüchow, J. B. Anderson, and D. Feller, ***J. Chem. Phys.*** 106, 7706 (1997).

[b] Experimental harmonic frequencies are based on the force field of A. R. Hoy, I. M. Mills, and G. Strey, ***Mol. Phys.*** 24, 1265 (1972).

TABLE 14.3 VIBRATIONAL FREQUENCIES OF PYRIDINE[a]

Symmetry	HF/ 6–31G	HF/ 6–311++G	HF/ 6–311++G (scaled)	B3LYP/ 6–31G	B3LYP/ 6–311++G	Experiment
A2	450	444	400	391	386	380
B1	481	478	430	433	430	406
A1	680	674	607	629	629	603
B2	737	731	658	682	681	654
B1	807	840	756	735	732	703
B1	856	796	716	774	765	747
A2	1,022	1,008	907	918	915	884
B1	1,096	1,078	970	974	969	941
A1	1,094	1,077	969	1,005	996	991
A2	1,160	1,135	1,022	1,018	1,010	980
B1	1,183	1,153	1,038	1,042	1,029	1,007
A1	1,138	1,125	1,013	1,059	1,049	1,030
B2	1,175	1,156	1,040	1,093	1,079	1,069
A1	1,192	1,178	1,060	1,109	1,099	1,069
B2	1,253	1,223	1,101	1,212	1,199	1,146
A1	1,354	1,339	1,205	1,262	1,249	1,217
B2	1,336	1,317	1,185	1,300	1,271	1,227
B2	1,522	1,507	1,356	1,416	1,405	1,355
B2	1,614	1,594	1,435	1,492	1,478	1,437
A1	1,659	1,639	1,475	1,526	1,512	1,483
B2	1,776	1,752	1,577	1,625	1,604	1,574
A1	1,785	1,759	1,583	1,630	1,610	1,581
A1	3,369	3,332	2,999	3,198	3,163	3,025
B2	3,382	3,345	3,011	3,200	3,168	3,034
A1	3,391	3,353	3,018	3,210	3,178	3,057
B2	3,402	3,366	3,029	3,222	3,188	3,079
A1	3,412	3,375	3,038	3,233	3,199	3,070

[a] HF/6–311++G and experimental results adapted from W.-H. Yang and G. C. Schatz, *J. Chem. Phys.* 3831 (1992).

$$H + H_2 \rightarrow H\text{-}H\text{-}H \rightarrow H_2 + H$$

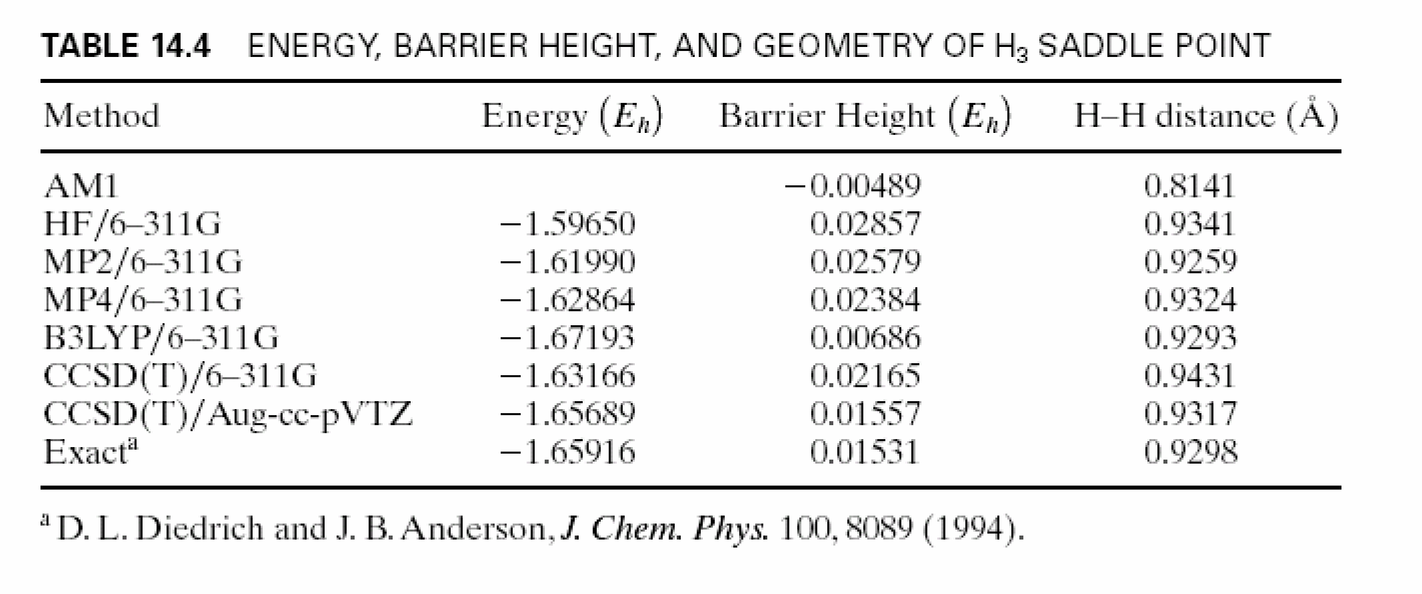


TABLE 14.4 ENERGY, BARRIER HEIGHT, AND GEOMETRY OF H_3 SADDLE POINT

Method	Energy (E_h)	Barrier Height (E_h)	H–H distance (Å)
AM1		−0.00489	0.8141
HF/6–311G	−1.59650	0.02857	0.9341
MP2/6–311G	−1.61990	0.02579	0.9259
MP4/6–311G	−1.62864	0.02384	0.9324
B3LYP/6–311G	−1.67193	0.00686	0.9293
CCSD(T)/6–311G	−1.63166	0.02165	0.9431
CCSD(T)/Aug-cc-pVTZ	−1.65689	0.01557	0.9317
Exact[a]	−1.65916	0.01531	0.9298

[a] D. L. Diedrich and J. B. Anderson, *J. Chem. Phys.* 100, 8089 (1994).

TABLE 14.5 VERTICAL EXCITATION ENERGIES (IN eV) ASSOCIATED WITH THE LOWEST EXCITED STATES OF THE WATER MOLECULE

State	CIS/6–311G(d)	Other theory	Experimental
$^1B_1$	8.74	7.52[a], 7.55[b], 7.60[c]	7.42[d], 7.49[e], 7.70[f]
$^1A_2$	10.55		9.1–10.2[g]
$^1A_1$	11.30		

[a] (CEPA), V. Staemmler and A. Palma, *Chem. Phys.* 98, 63 (1985).

[b] (CCSD), A. Balkava and R. J. Bartlett, *J. Chem. Phys.* 99, 7907 (1993).

[c] (CASSCF+SDCI), G. C. Schatz, A. Papaioannou, L. A. Pederson, L. B. Harding, T. Hollebeek, T.-S. Ho and H. Rabitz, *J. Chem. Phys.* 2340 (1997).

[d] H. T. Wang, W. S. Felps, and S. P. McGlynn, *J. Chem. Phys.* 67, 2614 (1977).

[e] K. Watanabe and A. S. Jursa, *J. Chem. Phys.* 41, 1650 (1964).

[f] M. L. Doublet, G. J. Kroes, E. J. Baerends, and A. Rosa, *J. Chem. Phys.* 103, 2538 (1995).

[g] This is the spectral range (including zero-point energy corrections) associated with the transition. See E. Segev and M. Shapiro, *J. Chem. Phys.* 77, 5604 (1982).

TABLE 14.6 VERTICAL EXCITATION ENERGIES (IN eV) ASSOCIATED WITH THE LOWEST EXCITED STATES OF PYRIDINE

State	CIS/6–311G(d)	ZINDO[a]	HAM[b]	Experiment[c]
$^1B_1$	5.83	4.37	4.9	4.59
$^1B_2$	6.45	4.78	4.9	4.99
$^1A_2$	7.15	5.36		
$^1A_1$	6.74	5.72	6.2	6.38

[a] W.-H. Yang and G. C. Schatz, *J. Chem. Phys.* 97, 3831 (1992).

[b] E. Lindholm and A. Asbrink, *Molecular Orbitals and Their Energies Studies by the Semiempirical HAM Method* (Springer, Berlin, 1985).

[c] A. Bolovinos, P. Tsekeris, J. Philis, E. Pantos, and G. Audritsopoulos, *J. Mol. Spectrosc.* 103, 240 (1984).

TABLE 14.7 STRUCTURES AND ENERGIES ASSOCIATED WITH $(HF)_2$

Method	Energy	r_b	r_f	R_{FF}	θ_b	θ_f	D_e
MP2/6–31G	−200.23664	0.9501	0.9516	2.7112	14.3	73.8	0.0127
MP2/large[a]		0.9264	0.9233	2.747	6.0	67.6	0.0072
CCSD(T)/large[b]		0.923	0.921	2.74	7	70	0.0075
Experiment[c]		0.923	0.920	2.736	7	68	0.00730 ±0.0001

[a] The basis set is a variant on aug-cc-pVTZ, as reported by W. Klopper, M. Quack, and M. A. Suhm, *Chem. Phys. Lett.* 261, 35 (1996).
[b] C. L. Collins, K. Morihashi, Y. Yamaguchi, and H. F. Schaefer, III, *J. Chem. Phys.* 103, 6051 (1995).
[c] B. J. Howard, T. R. Dyke, and W. Klemperer, *J. Chem. Phys.* 81, 5417 (1984).

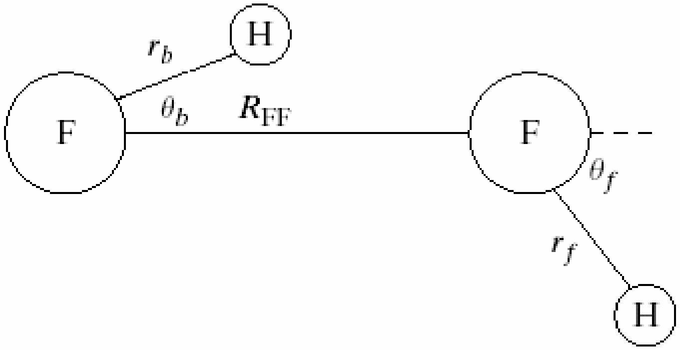


Figure 14.3 Structure of the HF dimer. Note that this structure is planar.

Solvation effects

Often one wants to learn about the properties of two interacting molecules, or a molecule plus a solvent. Including the other molecule or the solvent explicitly can be very time consuming, so an alternative is to do quantum mechanics on just the molecule, and then use classical electrostatics to describe the interaction with another molecule or with a solvent.

To do this it is convenient to describe the molecule in terms of effective charges on each atom, so that an electrostatic potential can be generated. Once the charges are known, the interaction with solvent can be described by solving the Poisson-Boltzmann equation (basic equation of electrostatics) to determine the electrostatic potential and from this the solvation energy.

Materials Fracture and Adhesion

Steven Mielke, Diego Troya, LiPeng Sun, Jeff Paci, Ted Belytschko, Sulin Zhang and George C. Schatz

Northwestern University

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Roberto Car - Princeton

Using Electronic Structure Theory to Model Mechanical Properties of Nanomaterials

- Nanotubes, rods and other nanomaterials provide the simplest systems for which mechanical properties (stress/strain behavior) can be measured.

- These materials provide an excellent opportunity to learn about the influence of defects and chemical functionalization.

- They are sometimes amenable to study using electronic structure theory methods, thus providing a platform for connecting fundamental theory with experiment.

Electronic Structure Theory will be used to:

- Establish shape of stress/strain curves, and their sensitivity to nanotube structure.
- Interpret experiments, establish theoretical limits.
- Examine the role of defects and chemical functionalization on fracture behavior.
- Integrate single nanotube results with bulk results.

Using electronic structure theory to describe fracture in nanosystems is a big challenge

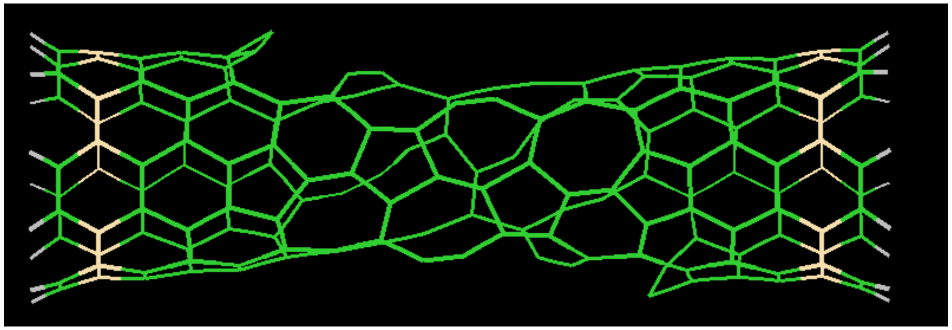
•Minimum size systems to model structure typically contain >100 atoms, and real systems are usually much larger.

•The quality of theory needs to be carefully considered: bonds are being broken, open-shell effects can be important, both finite cluster and periodic boundary conditions need to be considered.

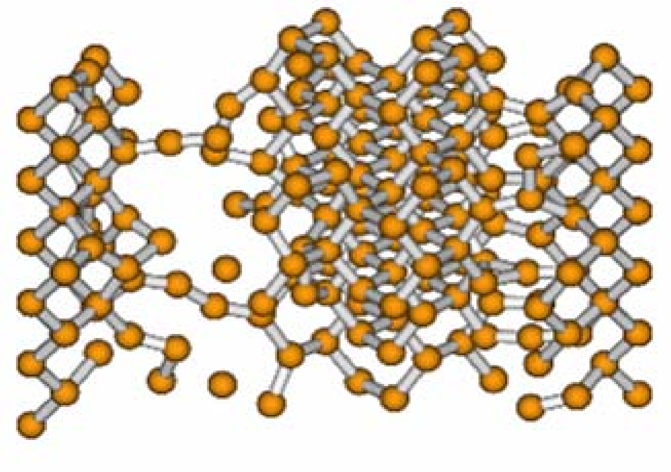
•Finite temperature effects might be important, but it is impossible to do useful MD calculations with most electronic structure models. Multiple pathways to fracture are possible.

Systems considered

Carbon Nanotubes (defects, chemical functionalization)



Ultrananocrystalline Diamond Films (grain boundary fracture, doping effects)



Electronic structure methods

DFT (PBE): SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms): a self-consistent DFT program. Highest accuracy of the methods we have studied, but computational effort is a serious problem.

PM3: Semiempirical method which is reasonably close to DFT for carbon-based nanostructures. Largely restricted to finite cluster calculations.

MSINDO: Semiempirical method that can be used both for clusters and for periodic boundary conditions. For carbon-based nanostructures it is less accurate than PM3.

SCC-DFTB (density functional-based tight-binding with self-consistent charges): an approximate DFT method.

Other methods

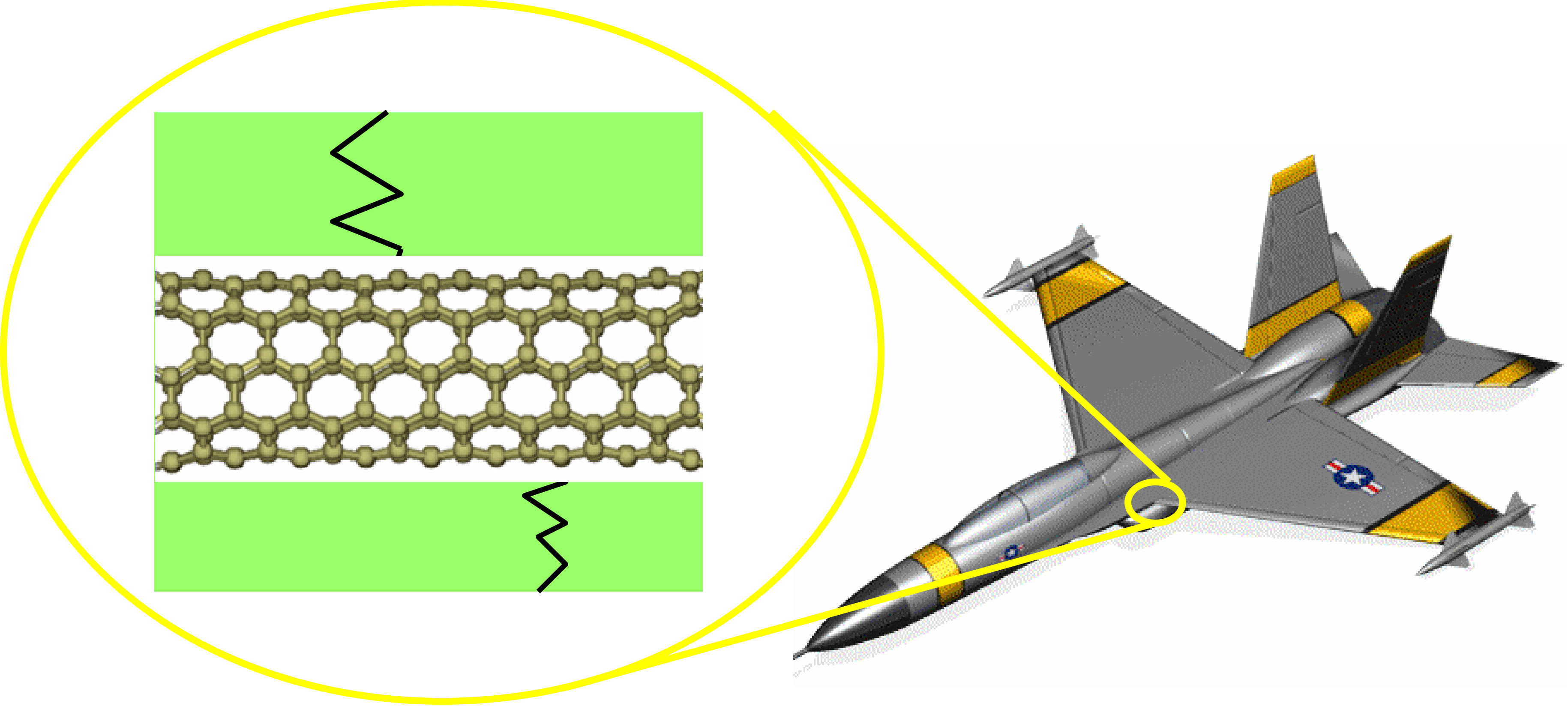
For systems with carbon and hydrogens, can use **Tersoff-Brenner** (reactive bond-order) potential for MM calculations.

Mixed **MM/CM** studies (and ultimately QM/MM/CM) to extend from a few atoms to a continuum description.

Carbon nanotube fracture

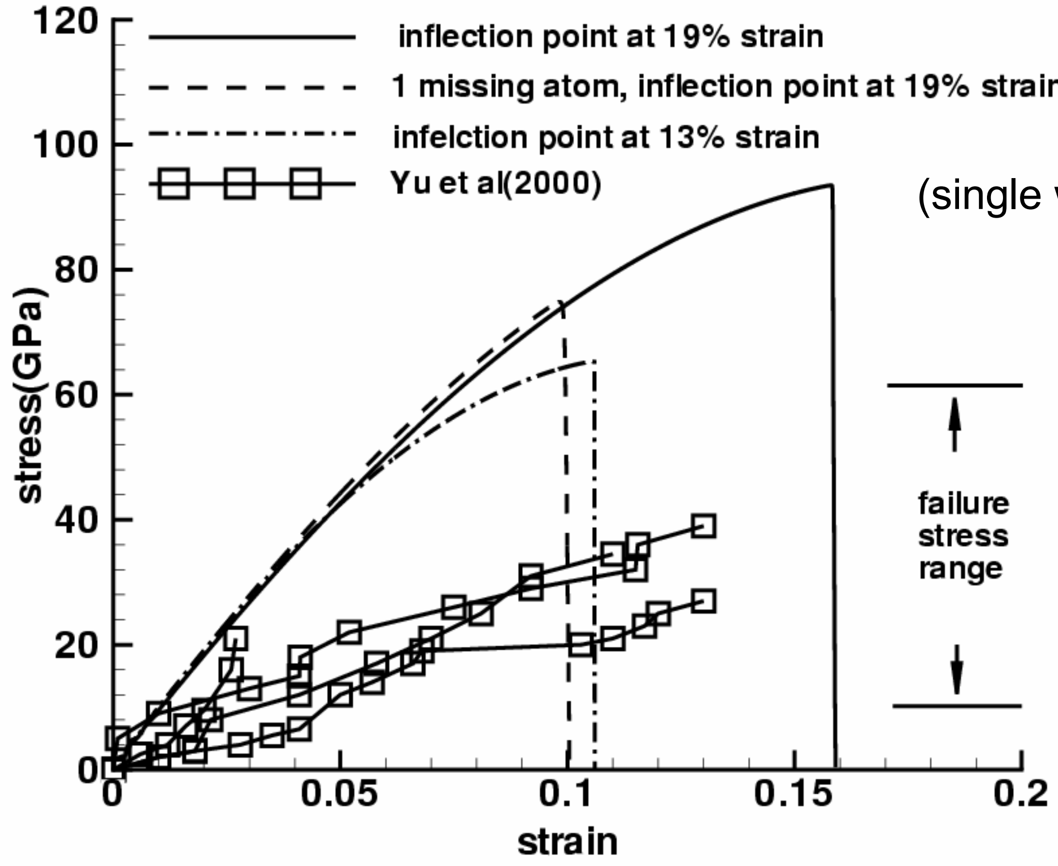
Carbon nanotubes are likely the strongest known materials

Their superior mechanical properties (resisting more than 1 order of magnitude larger tensile loads than reinforced steel) and their lightweight nature (six times less than steel) make them perfect candidates for reinforcement materials in nanocomposites



Fracture of Carbon Nanotubes
MM calculations with empirical force fields

T. Belytschko, S. P. Xiao, G. C. Schatz and R. Ruoff, Phys. Rev. B 65, 235430/1-/8 (2002).

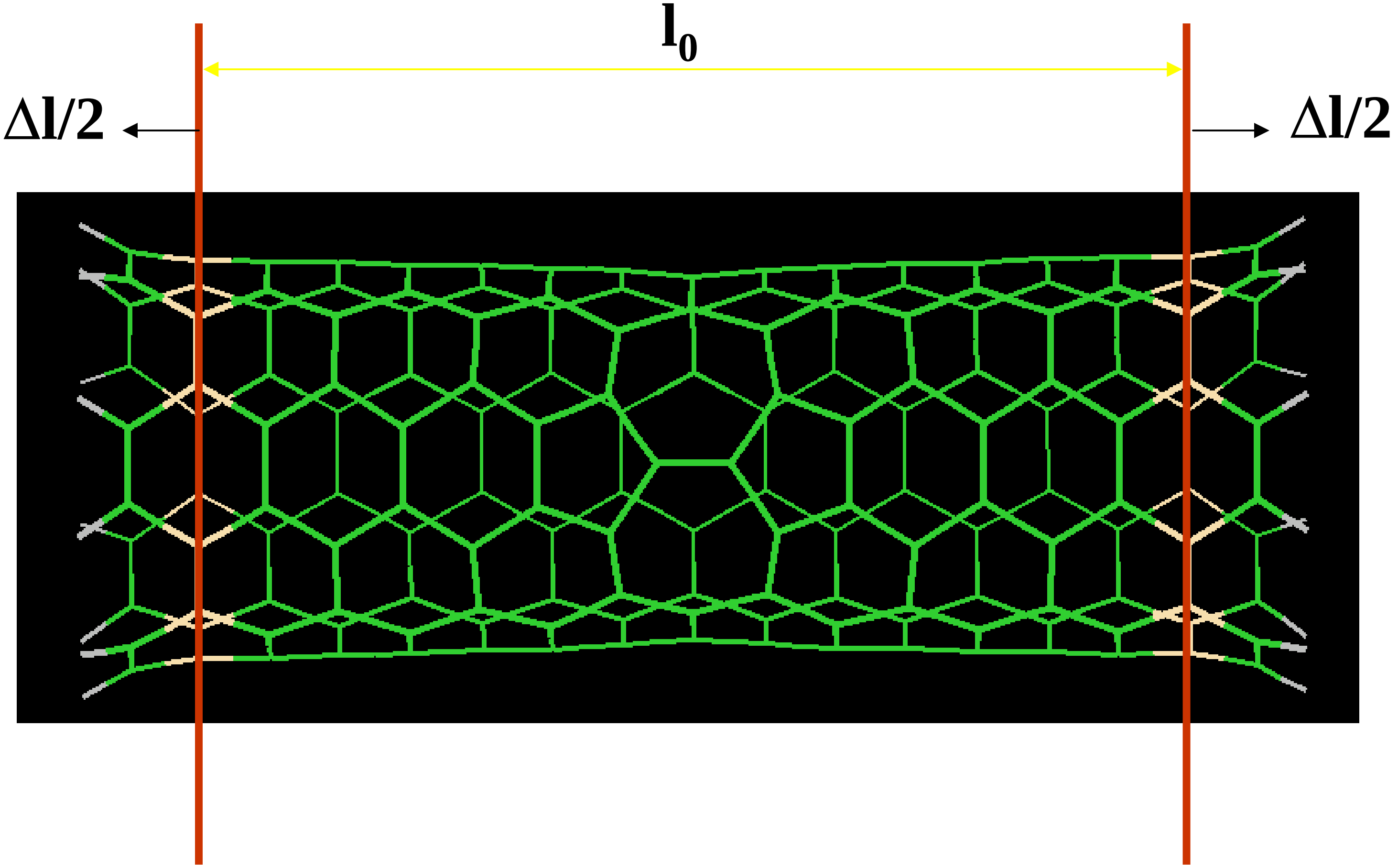


(single wall tube results)

(Multiwall tubes)

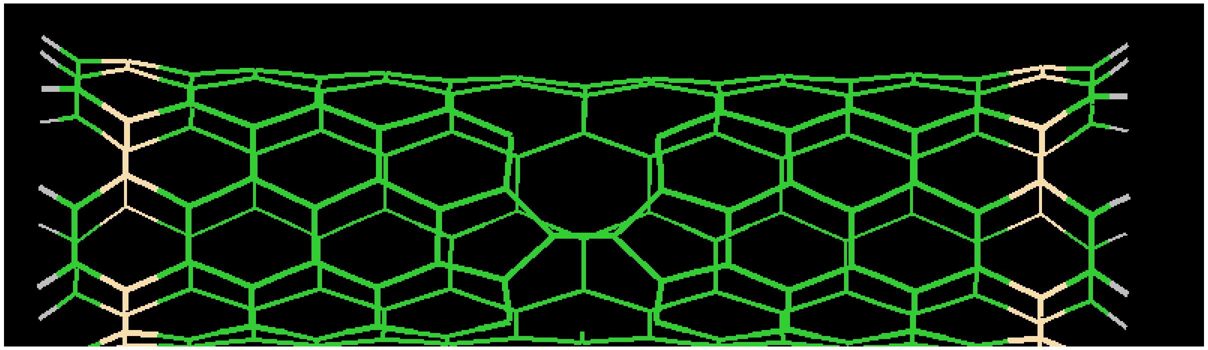
Carbon nanotube fracture

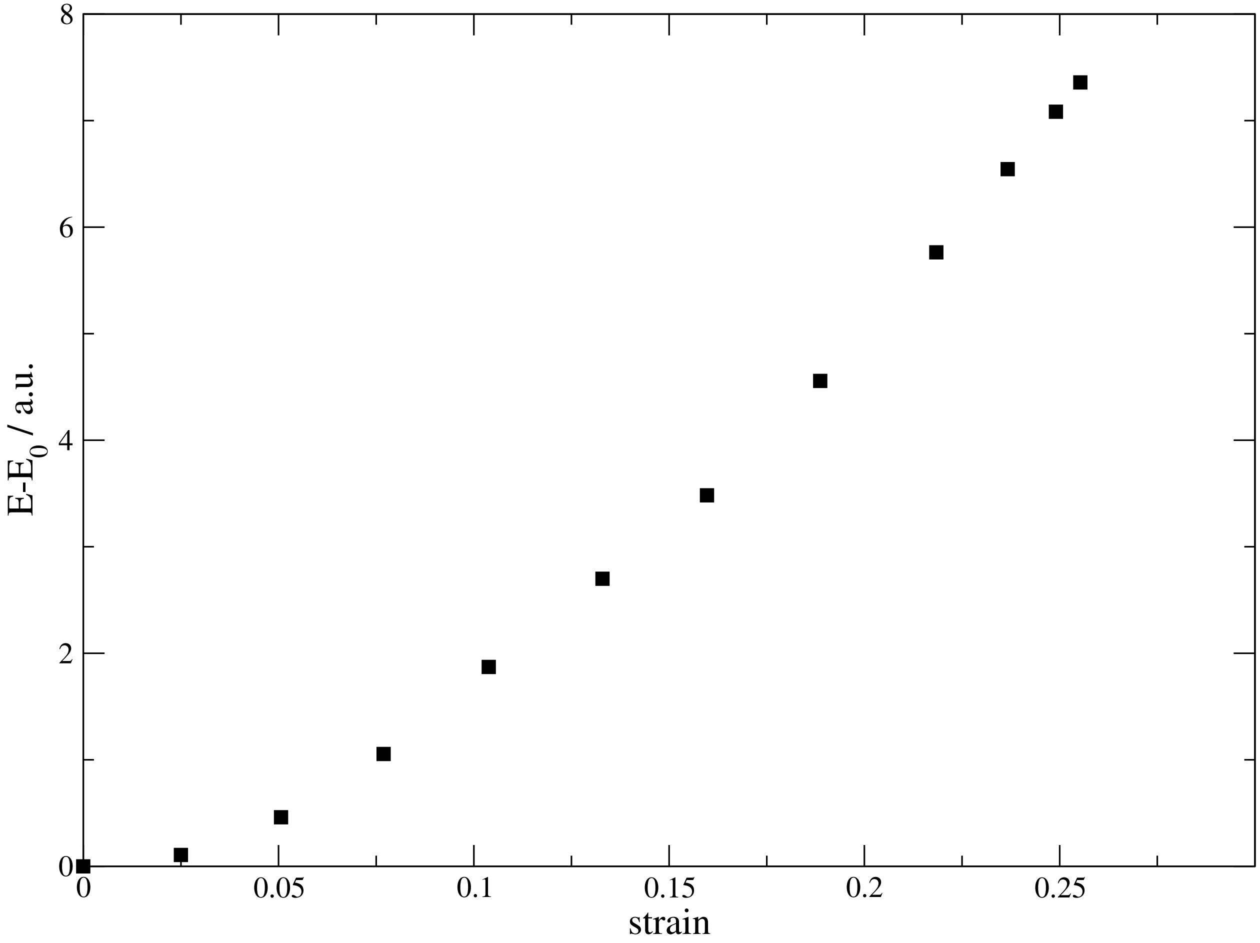
Determination of stress vs strain curve for [5,5] tube with Stone-Wales defect (170 carbon atoms)



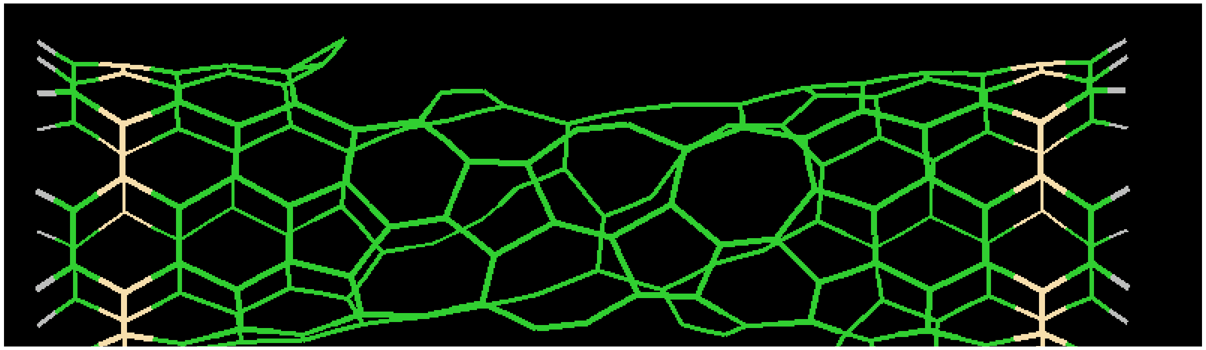
strain= $\Delta l/ l_0$

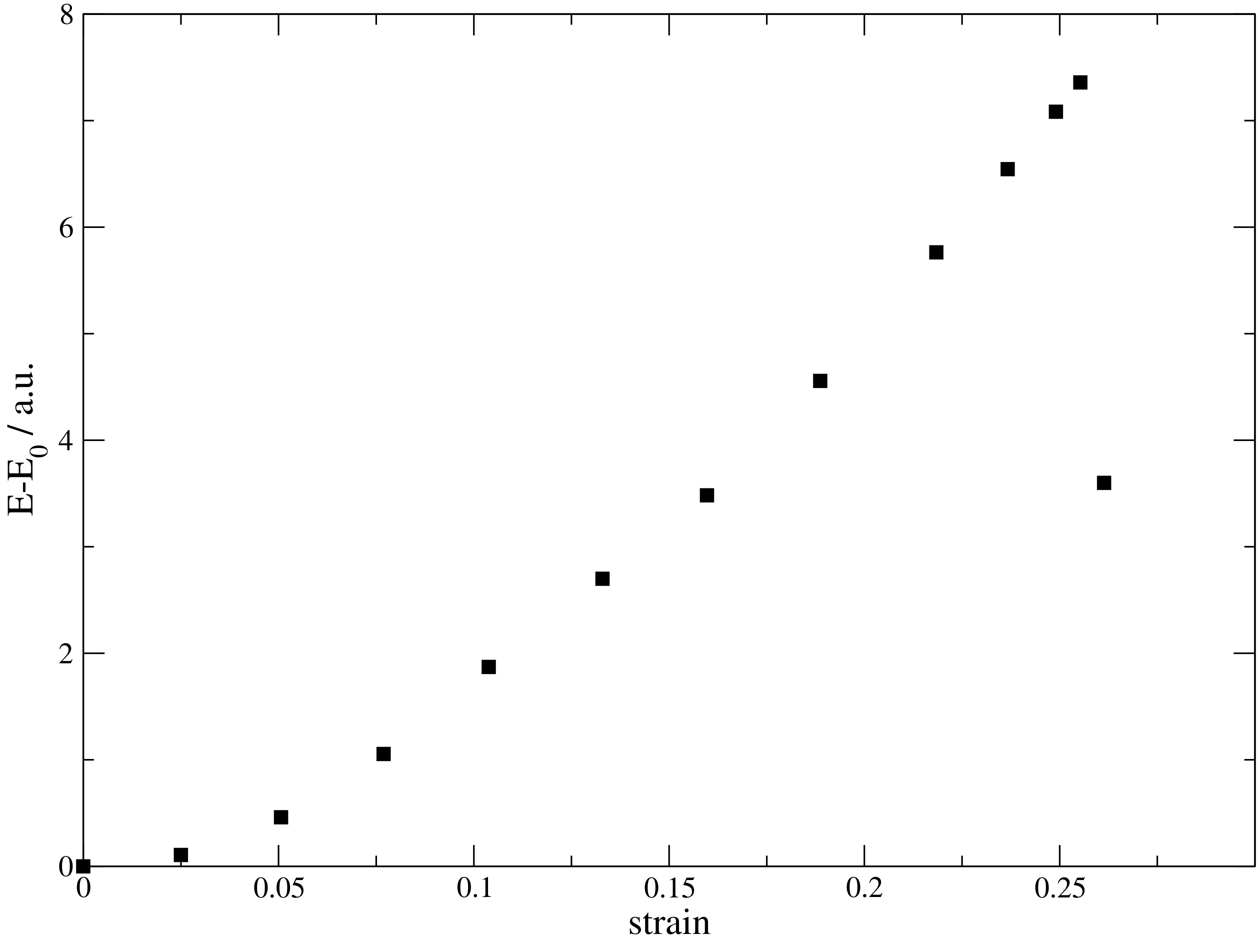
PM3 results: Strain = 0.255 (just before fracture)





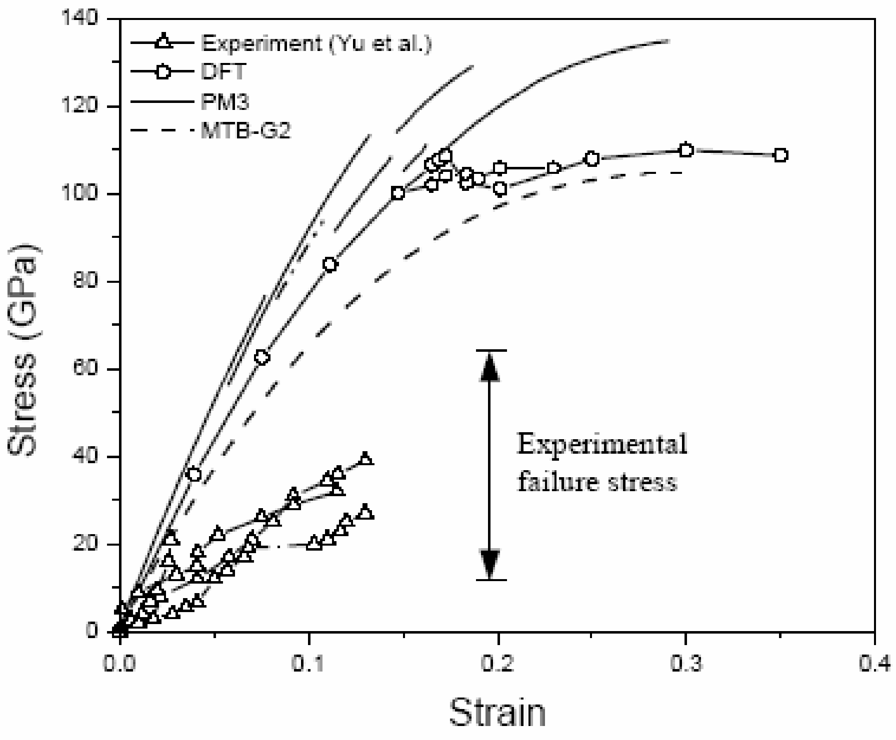
Strain = 0.26 (just after fracture)



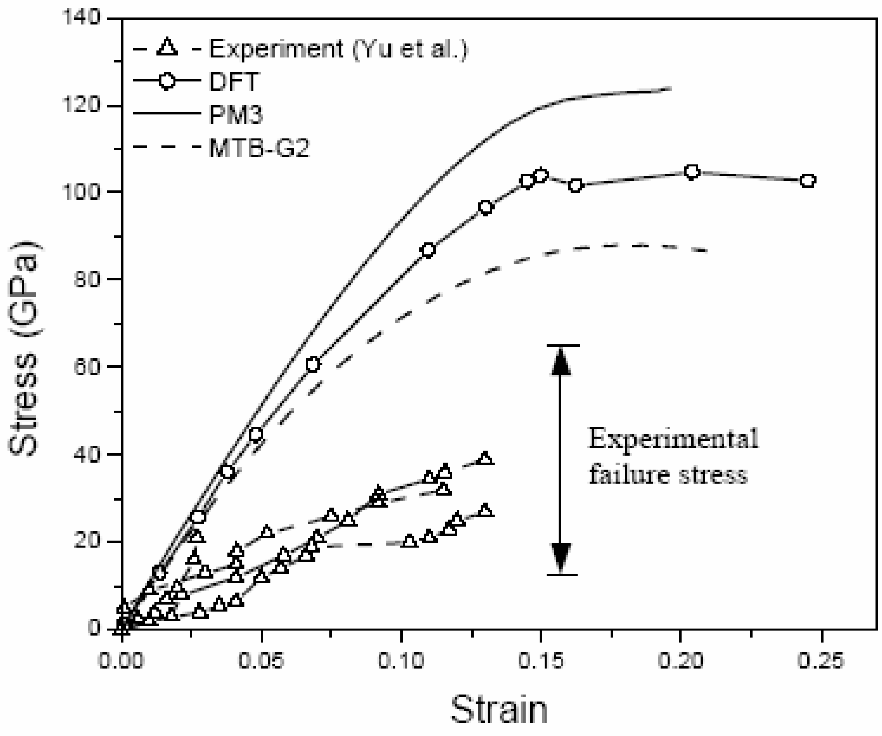


Stress-Strain Curves: undefected tubes

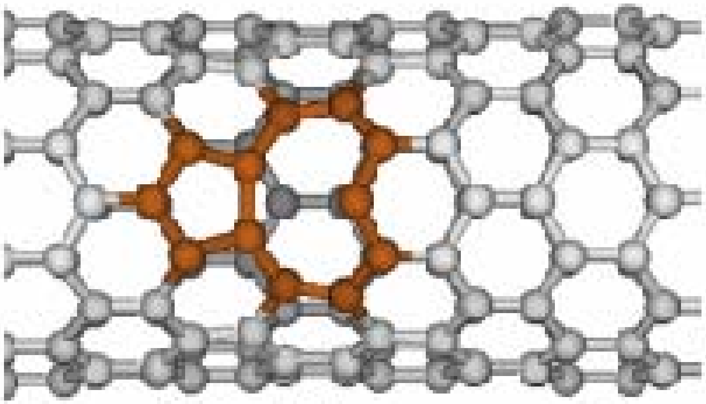
[5,5] tube



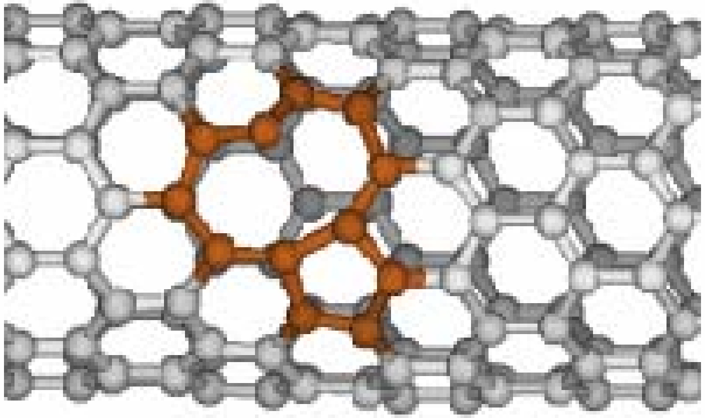
[10,0] tube



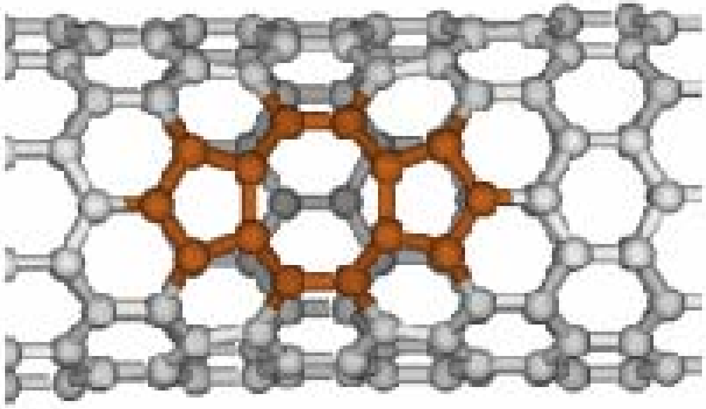
One and Two-Atom Vacancies



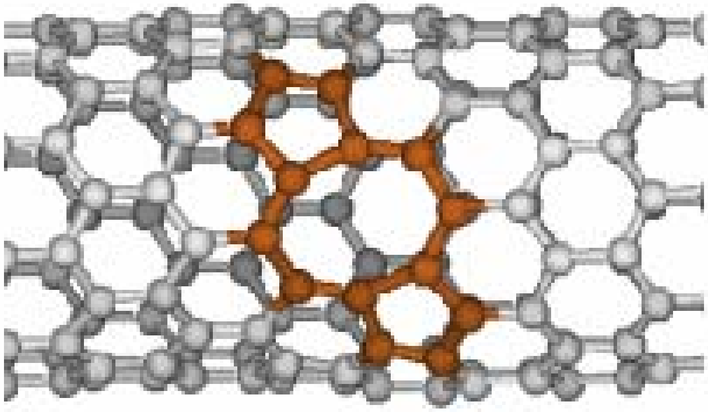
[10,0] 1 at. sym.



[10,0] 1 at. asym.

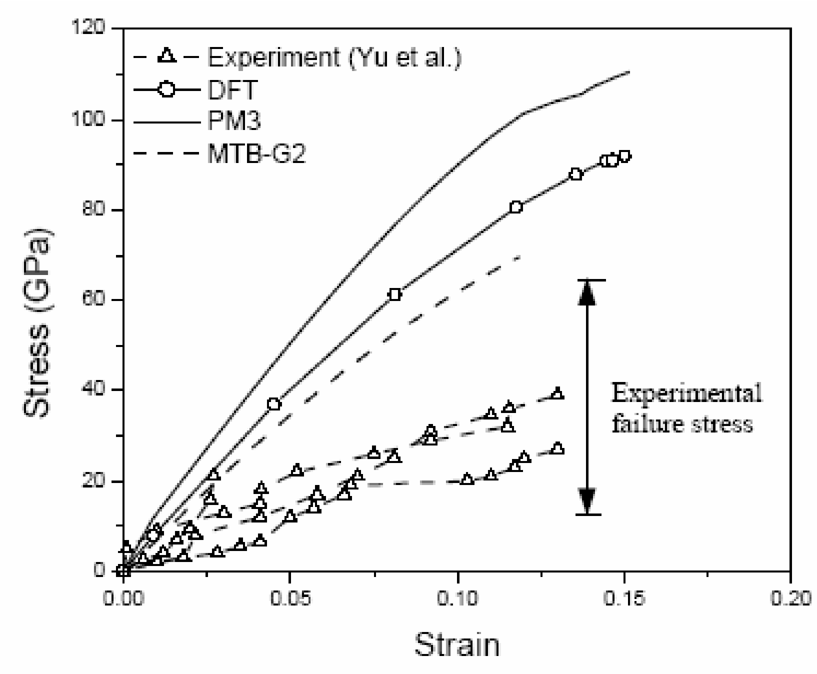


[10,0] 2 at. sym.

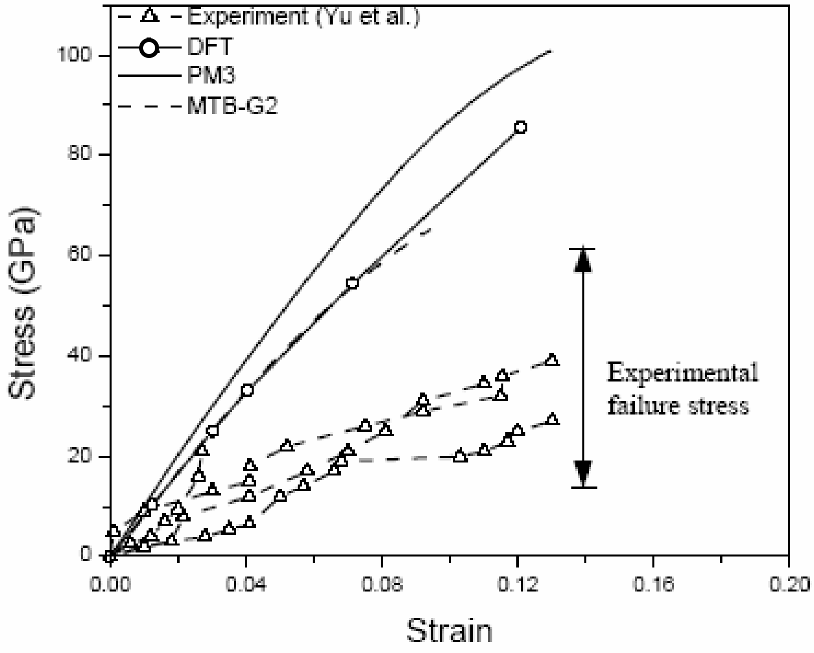


[10,0] 2 at. asym.

Fracture for one/two atom vacancies



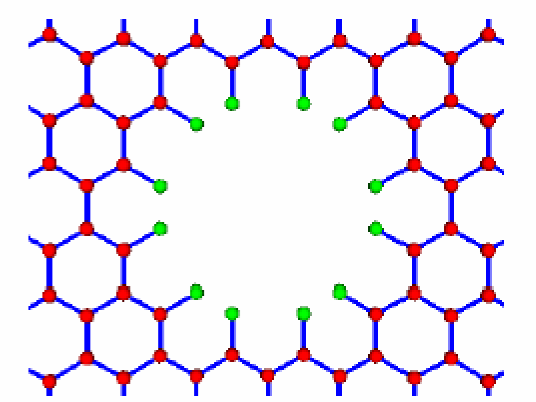
Two-atom vacancy (sym) [5,5] tube



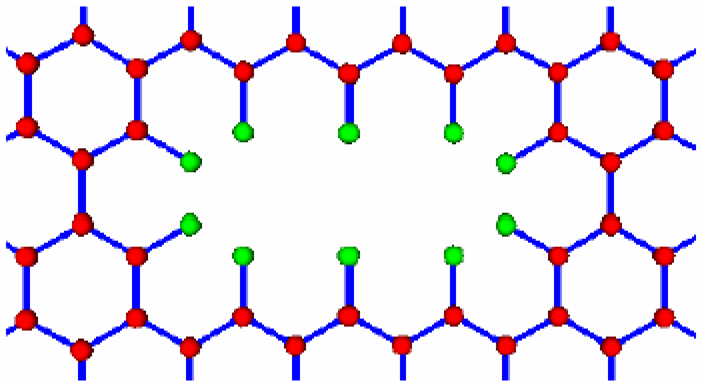
One-atom vacancy (asym), [10,0] tube

Fracture for Large Hole Defects

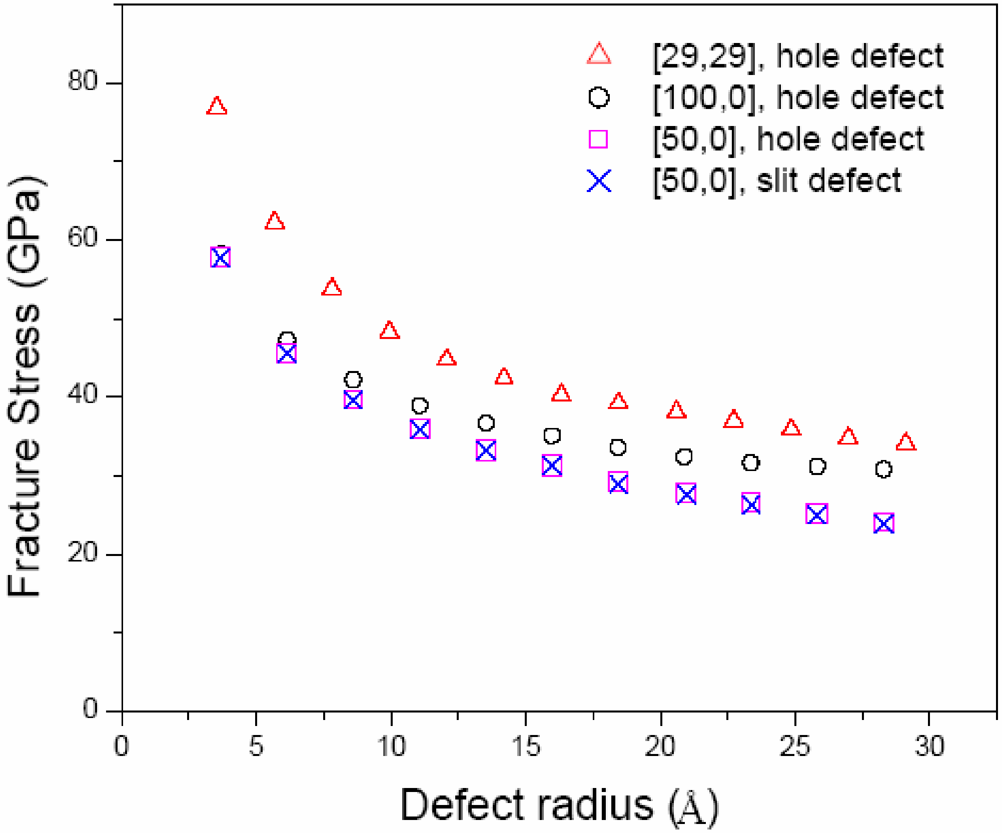
Hole Defect



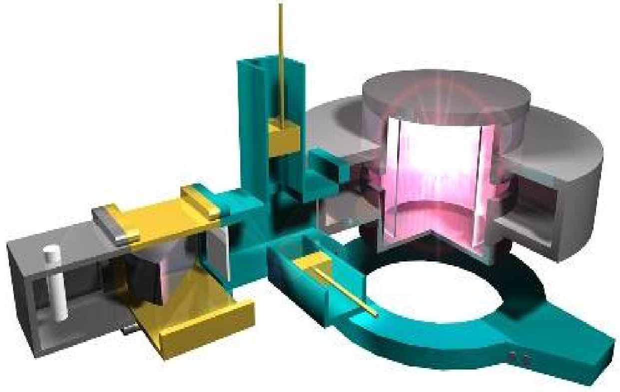
Slit Defect



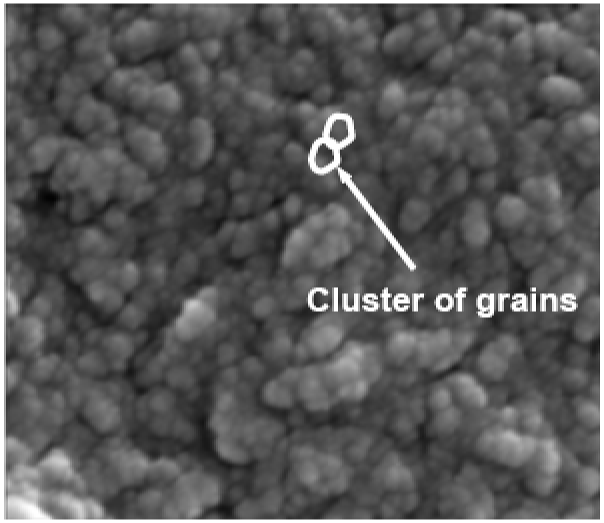
MM results

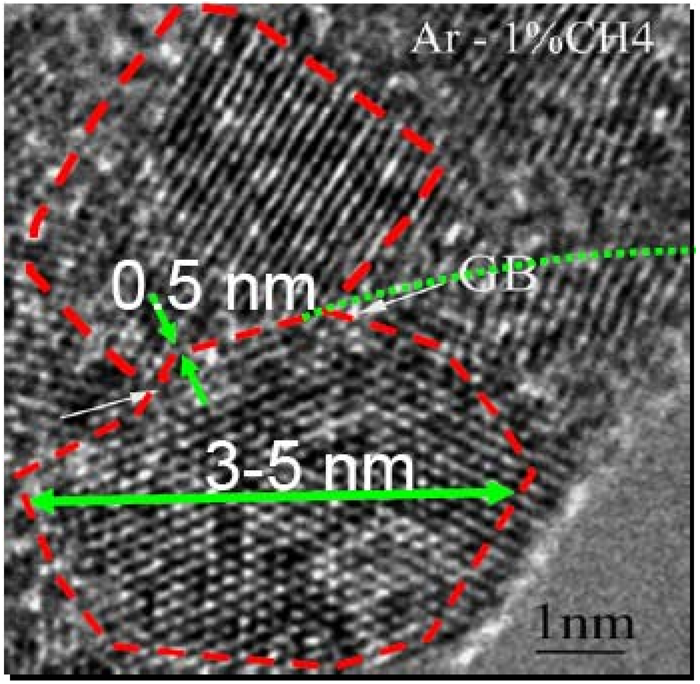


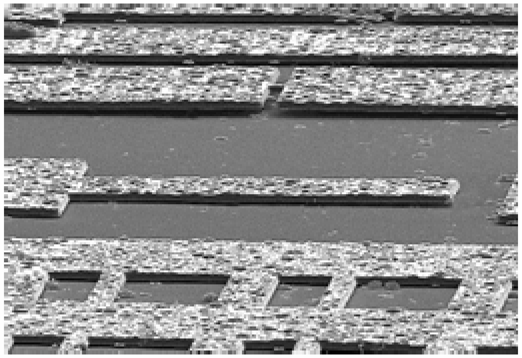
Ultrananocrystalline (UNCD) Diamond Films



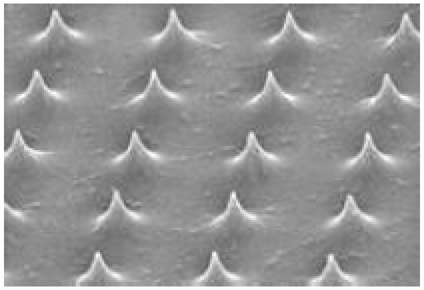
D. M. Gruen et al, Appl. Phys. Lett. 64 (1994) 1502: J. Vac. Sci. Tech. A13 (1995) 1628.







UNCD MEMS



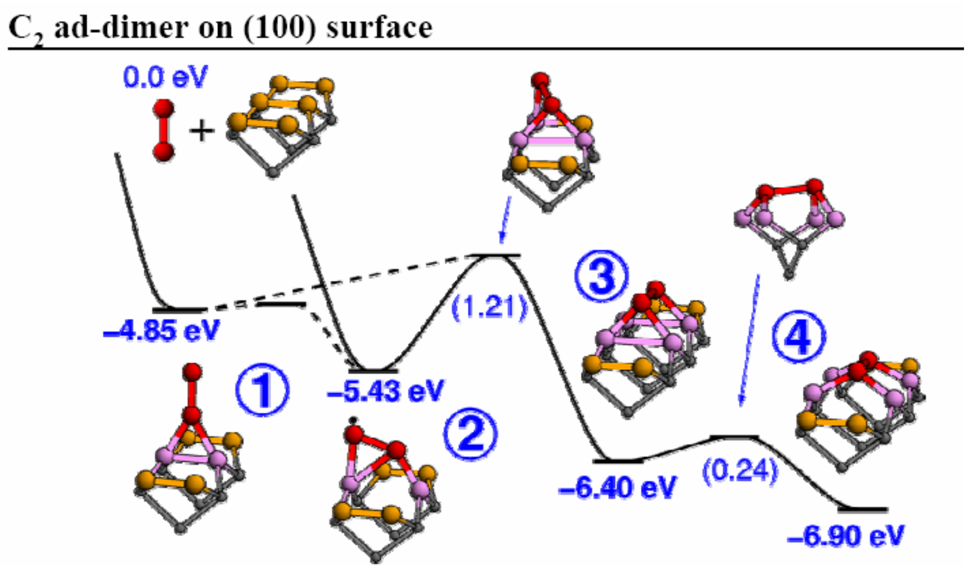
Field Emission

UNCD Structural Modeling

P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenheim, D. M. Gruen, Phys. Rev. B 65, 045403 (2002)

DF-TB (tight binding) studies of diamond film growth, and of grain boundary structures.

Σ13 grain boundary structure
67.4° twist perpendicular to 100 plane
208 atoms



C$_2$ ad-dimer on (100) surface

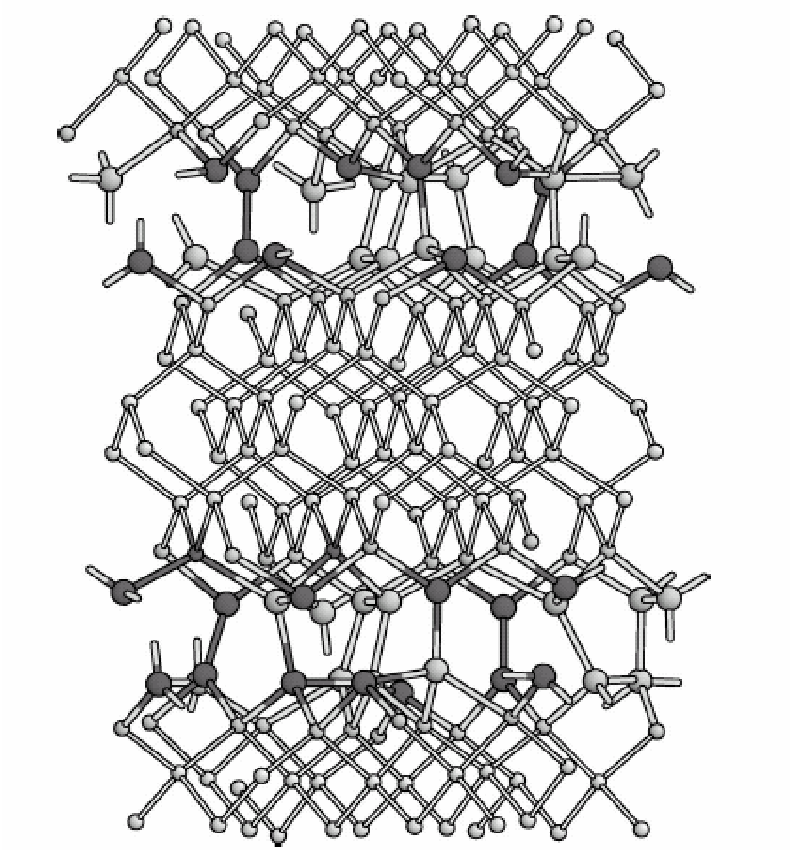
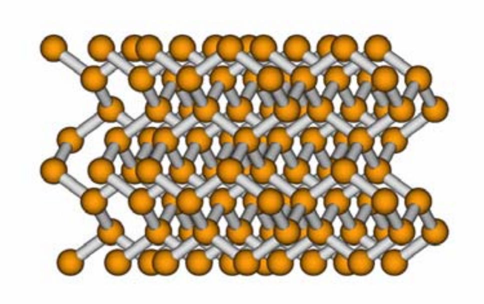
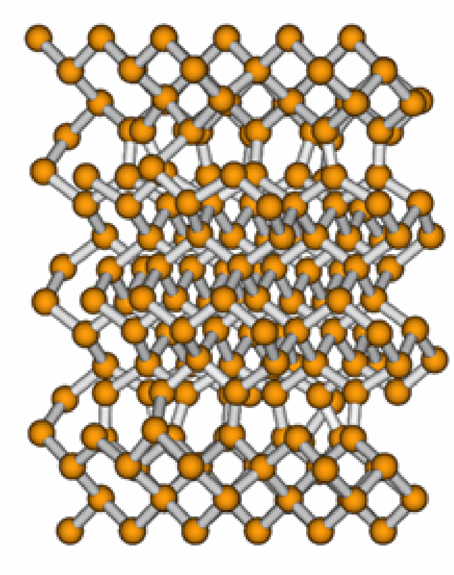


FIG. 1. Side view of the periodic cell for an optimized diamond Σ13 grain boundary. Two grain boundaries are shown. Black atoms are three-coordinated and gray atoms are four-coordinated. Atoms in the first layers of the interfaces are shown as larger spheres. Bonds extending across the cell boundary are shown as half bonds.

UNCD grain boundaries



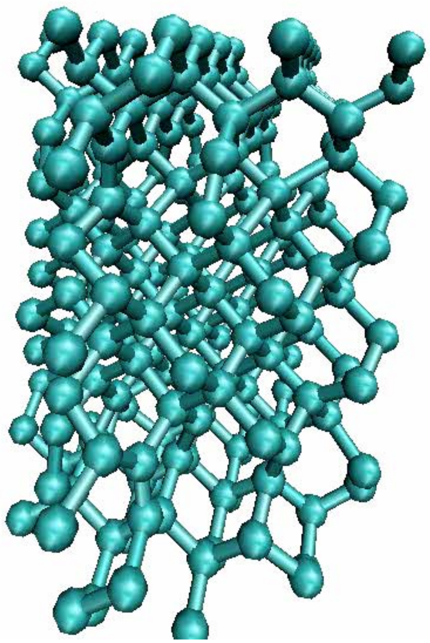
no GB



two GBs

UNCD fracture: PBE

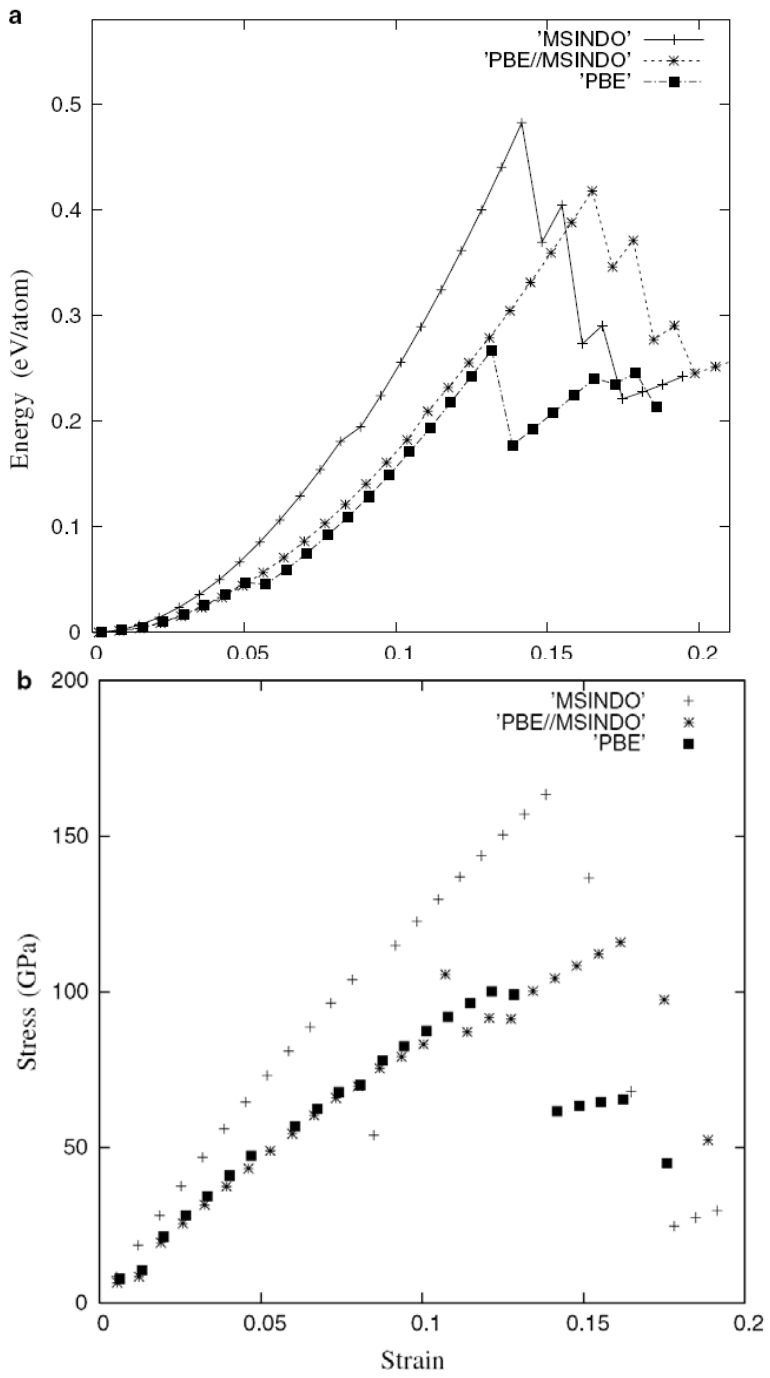
- Significant damage to both GB’s.
- Complete failure of the bottom GB.



UNCD: Results

- Energy/stress versus strain curves.
- Results produced using MSINDO (+), SIESTA to calculate the energy of the MSINDO structures (∗), and SIESTA using the PBE GGA functional (■).
- PBE//MSINDO is much better than MSINDO at capturing mechanical properties but predicts a qualitatively different fracture mechanism.

J. T. Paci et al., Chem. Phys. Lett. 414, 351 (2005).



Summary of mechanical properties

Cluster	E (TPa)	ϵ_f	σ_f (GPa)
Single-crystal (MSINDO)	1.56	0.34	277
Single-crystal (PBE//MSINDO)	1.01	0.37	219
Single-crystal (PZ)	1.09	0.36	239
Single-crystal (PBE)	1.09	0.35	233
UNCD (MSINDO)	1.53	0.14	163
UNCD (PBE//MSINDO)	0.955	0.16	116
UNCD (PBE)	1.05	0.13	100

E - the Young’s modulus (stiffness).
ε_f - failure strain.
σ_f - fracture stress.

PBE results are probably the most accurate.

Theoretical versus practical strengths

- Our *E* values of 1.09 and 1.05 TPa for single-crystal and UNC diamond, respectively, agree well with the corresponding experimental values of 1.05 and 0.95 TPa.
- Experimentally measured fracture stress values for single-crystal diamond and UNCD are $\sigma_f \sim 4$ GPa and $\sigma_f \sim 1\text{-}5$ GPa, respectively. We are way-off here. What we have left out is the effect of large (~100 nm) cracks.
- Cracks lead to regions of stress concentration which result in crack propagation and material failure.
- The effect of defects on the fracture behavior of a brittle material like diamond can be described using Griffith theory.

Griffith theory

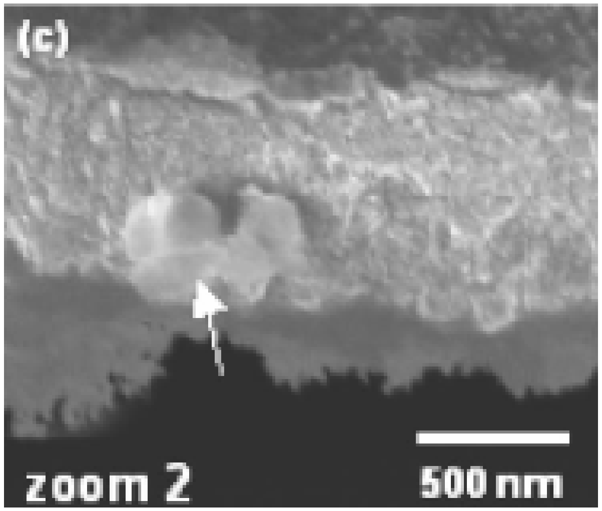
- Basic idea: when the strain energy released by fracture is larger than the energy required to create new surface (the surface energy), a crack will propagate.
- It can be shown that for a penny-shaped crack of radius *c,* the Griffith fracture stress is

$$\sigma_{\mathrm{f}} = \left(\frac{\pi E \gamma}{2c(1 - \nu^2)} \right)^{1/2},$$

where γ is the fracture surface energy and ν is the Poisson ratio. For UNCD, we calculated γ =2.6 J/m^2. For example, this means that for a crack with radius, *c* = 50 nm in a UNCD grain boundary, σ_f = 9.3 GPa.

Practical strength of UNCD

- Typical experimentally observed defects have radii, $c \sim 300$ nm.
- According to the Griffith equation, a crack with this radius will result in σ_f = 3.8 GPa, a value within the $\sigma_f \sim$ 1-5 GPa UNCD fracture stress range.

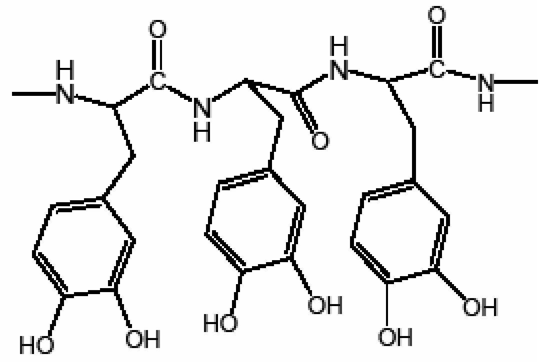


H. D. Espinosa et al., J. Appl. Phys. 94, 6076 (2003).

Computational modeling of bioadhesion

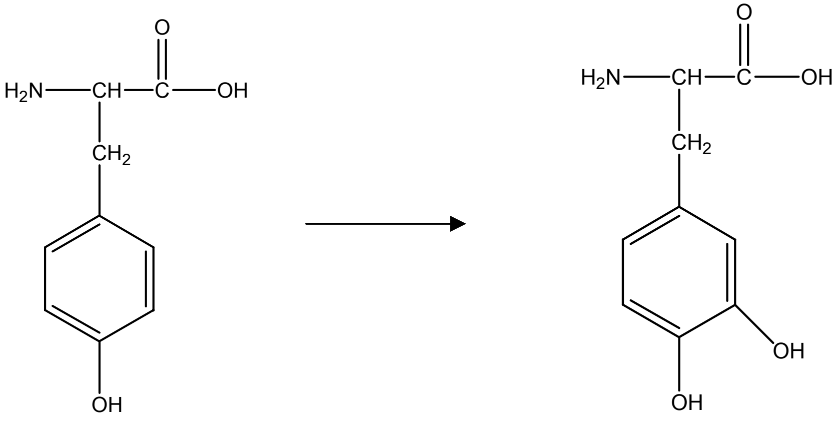
Fred Arnold, Linlin Zhao, George C. Schatz
in collaboration with Phil Messersmith

Mussel adhesive protein (MAP) contains an unusually high concentration of the DOPA amino acid residue.



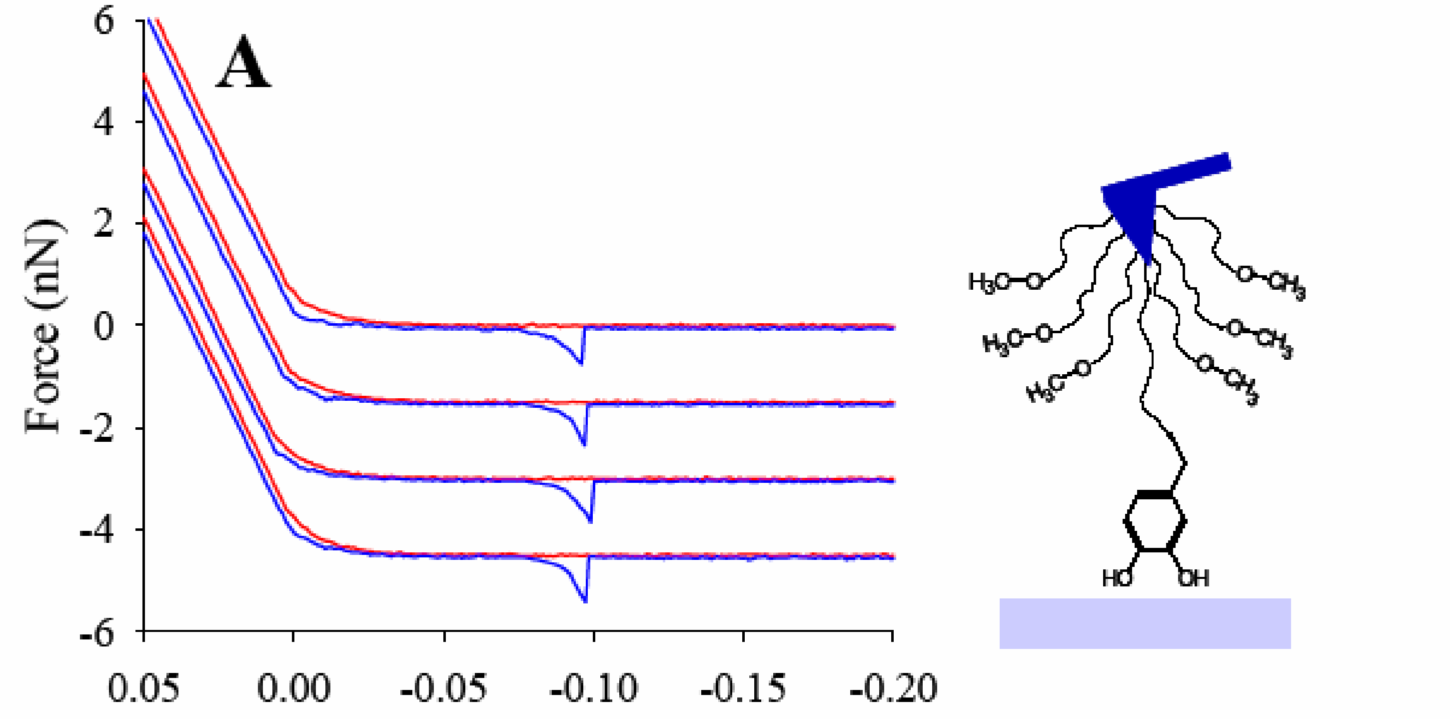
This is produced by hydroxylation of tyrosine (one of the standard amino acids).

Tyr



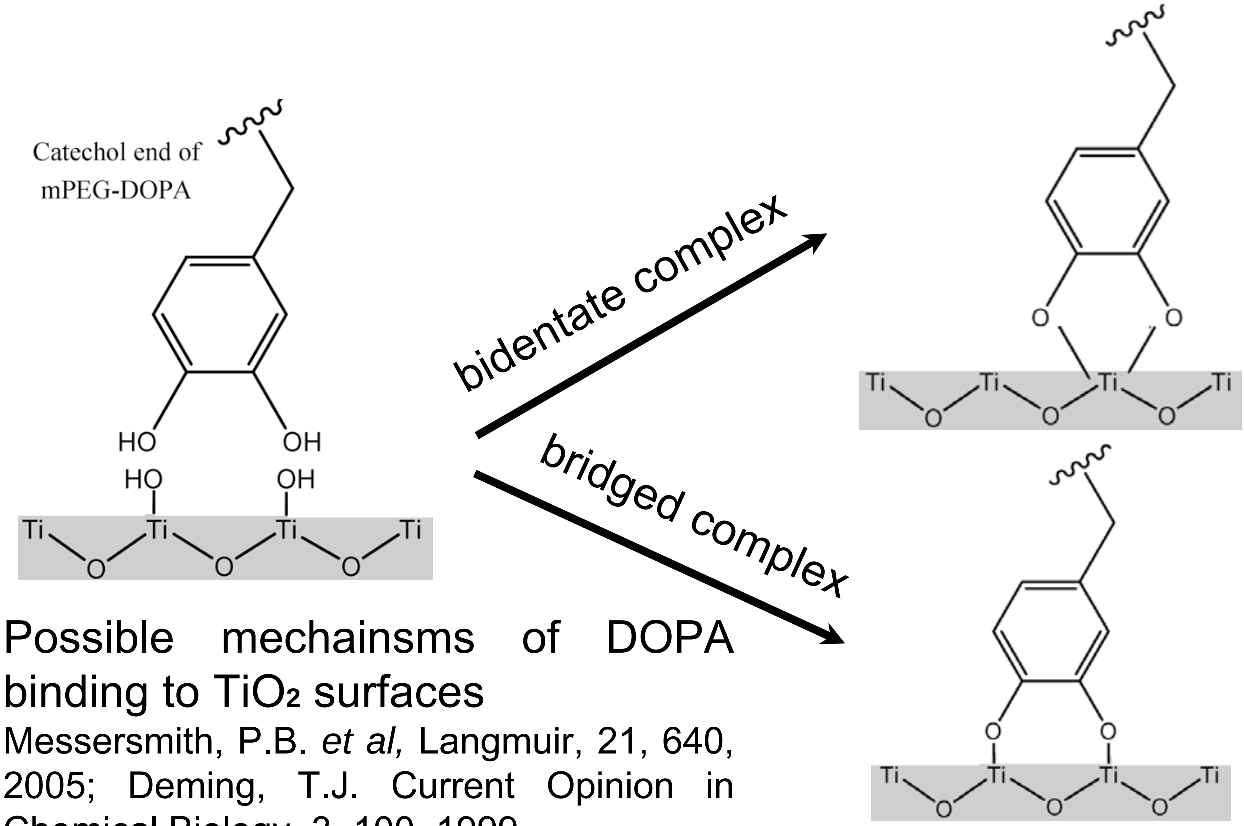
DOPA

Recently, Messersmith and coworkers have measured the force needed to pull-off a single DOPA-containing molecule from a TiO_2 surface. This corresponds to a 22 kcal/mol binding energy. (Lee, Scherer, Messersmith, PNAS submitted)



What is the mechanism of adhesion? Coordination complex, hydrogen bonds, pi-stack interaction, or a combination of these are all possible?

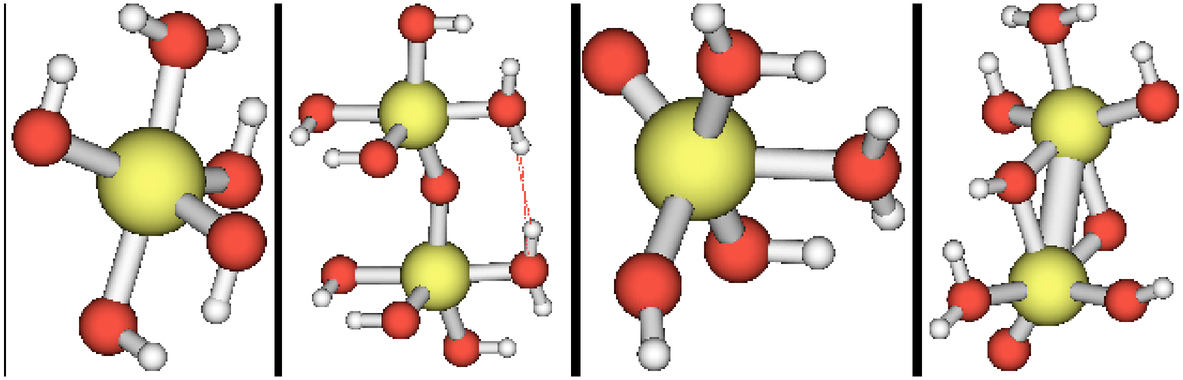
Proposed mechanisms for DOPA binding to TiO_2



Possible mechainsms of DOPA binding to TiO_2 surfaces

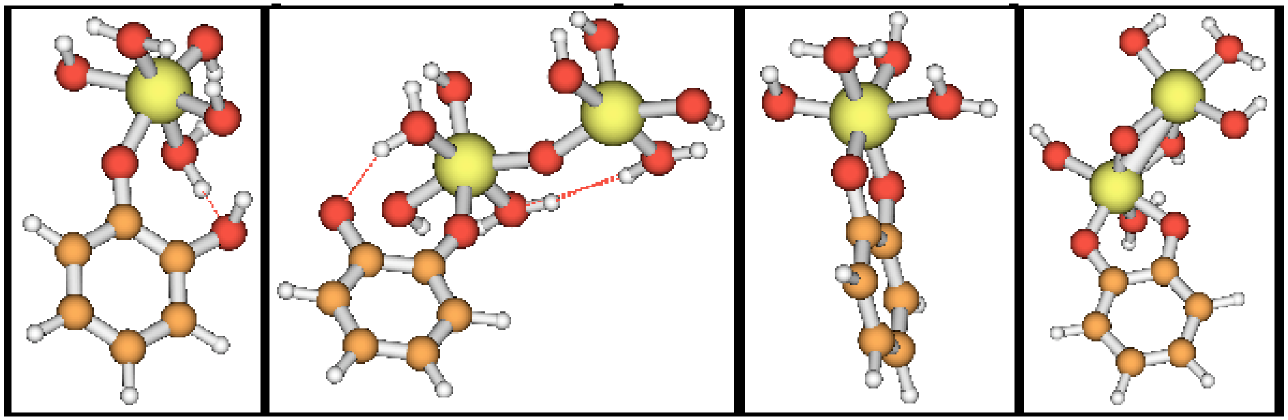
Messersmith, P.B. *et al,* Langmuir, 21, 640, 2005; Deming, T.J. Current Opinion in Chemical Biology, 3, 100, 1999

Cluster Models used to model the TiO_2 surface



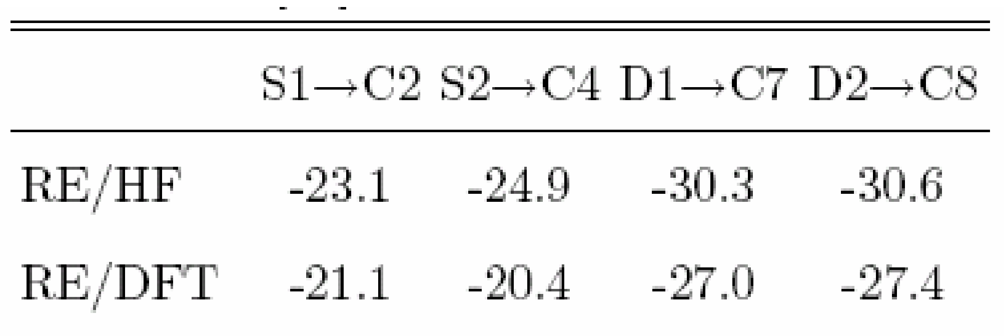
Cluster models used for TiO_2 absorption site : S1, S2, D1, D2

S1(2) + catechol ⟶ C2(4), D1(2) + catechol ⟶ C7(8) + H2O



Catechol-TiO_2 complexes: C2, C4, C7, C8

Binding energy (kcal/mol) of catechol at TiO_2 absorption site and defect $Ti=O_2$ double bond site, results obtained using GAMESS HF/6-31G*//B3LYP/6-31G*.



	S1→C2	S2→C4	D1→C7	D2→C8
RE/HF	-23.1	-24.9	-30.3	-30.6
RE/DFT	-21.1	-20.4	-27.0	-27.4

Bidentate structure is favored over monodentate structure, and binding energy is around 27 kcal/mol.

Further studies

- Calculate pull-off force to make comparisons with Messersmith measurements
- Compare DOPA, tyrosine and other amino-acids
- Compare TiO_2, SiO_2, Au and other surfaces to determine relative role of different adhesion mechanisms