Atomistic interaction models

- The true interaction energy between N nuclei and I electrons could be obtained by solving the Schrödinger equation for the system comprising the $N+I$ bodies.
  - This is assuming interactions between the nucleons and other effects and electrons can be neglected
    - This is almost always true
  - This is also assuming relativistic effects can be ignored
    - This is not always true for heavy elements (eg. Hg, Au)
    - For these one should and can use the Dirac equation instead

  - Solving the time-dependent equation would also give the atom and electron motion directly, without the need for MD algorithms at all

- But solving the full equation is extremely expensive computationally, and hence one always has to resort to various levels of approximation

- An overview of the type and speed of different interatomic force models and their efficiency:

Model	Type	Scaling	N_{max}[1]
Full solution of Schrödinger equation	quantum mechanical, ab initio	$O(e^N)$	1
HF (Hartee-Fock)	quantum mechanical, ab initio	$O(N^{4-8})$/ $O(N)$	50
DFT (density functional theory	quantum mechanical	$O(N^3)$/ $O(N)$	200
TB (Tight-binding)	quantum mechanical (often semiempirical)	$O(N^3)$/ $O(N)$	1000 10000
Many-body potential	classical, semiempirical	$O(N)$	10^7
Pair potential	classical, semiempirical	$O(N)$	10^7

[1]This is a very rough estimate of how many atoms N can be simulated in a reasonable time, i.e. a week or so, on a single-processor machine. For multi-electron atoms solution of the full Schrödinger equations is very hard even for a single atom.

- As indicated, there are nowadays $O(N)$ variants of all classes of methods. However, the quantum mechanical $O(N)$ methods are mostly only recently developed and work (so far) well only in a limited set of problems.

- This is not the full story, though: another aspect is of course the prefactor in the efficiency, i.e. the factor A in

$$\text{speed} = A \times N^x$$

for an $O(N^x)$ method. A rule-of-thumb estimate of the current typical state of affairs is:

$$A_{\text{manybodypotential}} = 3\ A_{\text{pairpot}}$$
$$A_{\text{tight-binding}} = 100\ A_{\text{manybodypotential}}$$
$$A_{\text{DFT or HF}} = 100\ A_{\text{tight-binding}}$$

- This is extremely rough, and varies a lot in different flavours, but gives the important insight: even a linear-scaling $O(N)$ DFT method is still going to be something like 10000 times slower than a classical method for the same N.

- The number of atoms available to quantum mechanical models (HF and DFT) ~ 100 is enough to simulate e.g. small molecules, bulk properties of common phases, and point defect properties.

- Tight-binding is a “minimal quantum mechanical” model which works well in a few materials (e.g. C, Si, Ge) but is problematic in many others.

- With classical models it is nowadays possible to simulate even very large systems, such as large protein molecules, 2- and 3-dimensional defects, whole nanoclusters, surface growth, grain boundaries etc. etc. The main limitation is that they do not usually directly give information on the electronic properties of the material.

- Here we will only outline some main features of the quantum mechanical models, as a comprehensive treatment is well beyond the scope of this course. The idea is that you should at least know some central terminology and which kind of model suits to which kind of system.

  - Much more info about the quantum mechanical methods is given on the course Electronic structure calculations, to be lectured next time in 2004-2005

Overview of quantum mechanical models

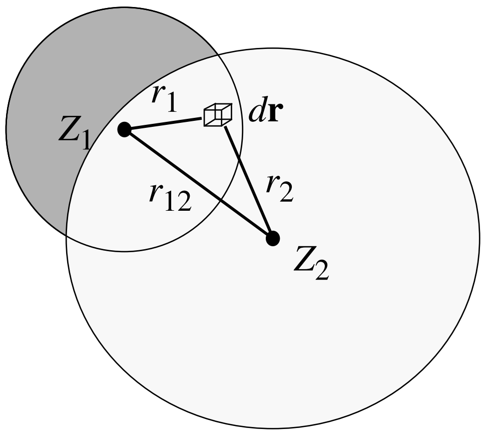
Schrödinger equation

$$H\Psi = E\Psi$$

where the Hamiltonian operator H can be written for a system of N nuclei and I electrons (which have coordinates $\mathbf{r}_n$ $(n = 1 \ldots N)$ and $\mathbf{r}_i$ $(i = 1 \ldots I)$):

$$H = \left(\overset{T_n}{-\sum_{n=1}^{N} \frac{h^2}{2M_n} \frac{\partial^2}{\partial \mathbf{r}_n^2}} \overset{T_e}{- \sum_{i=1}^{I} \frac{h^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2}} \overset{V_{ee}}{+ \frac{1}{2} \sum_{i=1}^{I} \sum_{j=1}^{I} \frac{e^2}{|\mathbf{r}_{ij}|}} \right. \tag{7.1}$$

$$\left. \underset{V_{ne}}{+ \sum_{n=1}^{N} \sum_{i=1}^{I} \frac{Z_n e^2}{|\mathbf{r}_{ni}|}} \underset{V_{nn}}{+ \frac{1}{2} \sum_{l=1}^{N} \sum_{n=1}^{N} \frac{Z_n Z_l e^2}{|\mathbf{r}_{nl}|}} \right)$$



Here:

- T_n is the kinetic energy of the nuclei
- T_e is the kinetic energy of the electrons.
- V_{ee} , V_{ne} and V_{nn} are the electron-electron, electron-nucleus and nucleus-nucleus Coulomb interactions.

Hence we can write the Schrödinger eq. formally as:

$$-T_n - T_e + V_{ee} + V_{ne} + V_{nn}\Psi = E\Psi \tag{7.2}$$

Ψ is the total wavefunction of the full nucleus-electron system.

Born-Oppenheimer approximation

- Quantum mechanical simulations almost always start with the Born-Oppenheimer approximation. Roughly speaking this means simply that because the atoms are much heavier than the electrons, they also move much slower. Then for any given configuration of the nuclei one can assume that the electrons find their ground state before the atoms move significantly. In this case it is possible to solve the Schrödinger equation by assuming that the atoms do not move (you "nail down the atoms").

  - In fact also all classical simulations are based on the Born-Oppenheimer approximation, in the sense that the interatomic potentials do not depend on the atom motion.

- Mathematically speaking this means that the wavefunction Ψ for both atoms and electrons is separated into a product

$$\Psi \approx \psi(n, \mathbf{r}_i)\eta(n) \quad ,$$

where $\psi(n, \mathbf{r}_i)$ is the wave function of the electrons, which is a function of the positions of the electrons $\mathbf{r}_i$ and the positions of the nuclei n, and $\eta(n)$ is the wave function of the nuclei. Then $\psi(n, \mathbf{r}_i)$ fulfils the wave equation

$$\{-T_e + V_{ee} + V_{ne}\}\psi(n, \mathbf{r}) = E_e(n)\psi(n, \mathbf{r}) \tag{7.3}$$

where V_{ne} is the nucleus-electron potential of the original Hamilton operator. Solution of this gives the electronic total energy of the system, and can also be used to give the forces acting between atoms. Then the atom motion can be simulated using the classical MD algorithm

Hartree-Fock methods

- In the Schrödinger equation (7.3) the computationally most difficult part os the electron-electron interaction

$$V_{ee} = \sum_i \sum_j \frac{e^2}{|\mathbf{r}_{ij}|}$$

  which is a double sum from all electrons to all electrons. This can not be treated directly except in very small systems (of the order of one He atom...)

- The basic solution in Hartree-Fock (as well as density-functional theory) is to create some sort of "average" electron density with which every electron interacts independently. Then a double sum is replaced by a simple sum

$$V_{ee}' = \sum_i V_i^{av}$$

- In order that the total wave function ψ would fulfil the Pauli rule, it is written as a Slater determinant of one-electron wave functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \ldots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \ldots & \phi_2(\mathbf{r}_N) \\ . & . & . & . \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

- Hence the Schrödinger eq. for electrons reduces to an equation to get a one-electron wave function ϕ_i:

$$\sum_i (T_{e,i} + V_{ne,i} + V_i^{av})\psi(x_1, x_2, \ldots, x_n) = E\psi(x_1, x_2, \ldots, x_n)$$

$$(T_{e,i} + V_{ne,i} + V_i^{av})\phi_i(x_1) = \hat{F}\phi_i(x_1) = \varepsilon_i\phi_i(x_1)$$

  where $\hat{F}$ is the so called Fock-operator. The equation is the so called **Hartree-Fock equation.**

Internal note: this taken mostly from http://www.caos.kun.nl/tutorials/camm/mopac/fred/ch52.html

- Thus the new central problem becomes to find a good form for the average potential V_i^{av}. Usually the solution is looked for by starting from some initial guess for the wave functions ϕ_i, plugging it into the equation, solving to get a new ϕ_i , and keeping on iterating until the solution does not change any more, i.e. until a S**elf-Consistent Field** has been found. The method is called HF-SCF.

  Solving the equation is done with numerical methods which have been developed and optimized during the last ~ 50 years.

- The eigenvalues of the energy ε_i have a clear physical interpretation: they correspond to the energy which is required to ionize an electron from its orbital, and hence are an experimentally measurable quantity.

- The molecular orbital (MO) of every electron ϕ_i is written as a sum over atomic orbitals (**LCAO - Linear Combination of Atomic Orbitals):**

$$\phi_i = \sum_{\mu} C_{i\mu}\chi_{\mu}$$

- One the important properties of the SCF method is that it fulfils the variational principle, that is, the eigenvalues of every inaccurate wave function is larger than that of the most accurate one. So the smallest found energy is also the 'most correct' one.

- In the most straightforward approach the atomic orbitals (**basis functions**) χ_μ can be so called Slater type orbitals (STO)

$$\chi = R(r)Y_{lm}(\theta, \varphi)$$

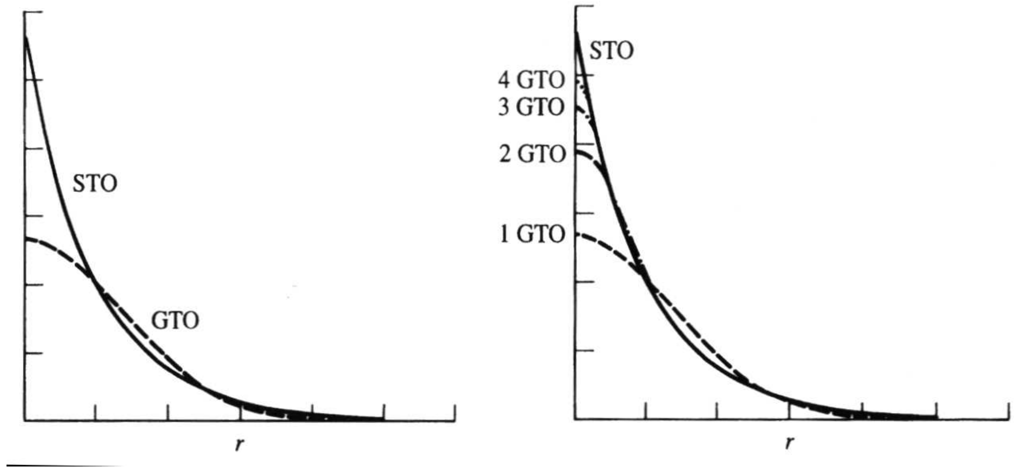
$$R_{1s} = N_1 e^{-\zeta r}$$

$$R_{2s} = R_{2p} = N_2 r e^{-\zeta r}$$

which clearly resemble orbitals of the hydrogen atom. Here ζ is a factor which describes the screening of the nuclei due to the electron cloud. Integrating these STO orbitals is numerically difficult, however. Computationally it is much more favourable to use Gaussian functions for the orbitals, i.e. **Gaussian-type orbitals (GTO).** But real electron wave functions are not Gaussian in shape, but closer to the STO shapes. Hence to obtain a realistic shape for the wavefunction one uses a sum of GTO's to describe one wave function of a real electron:

$$\chi^{GTO}(r) = e^{-\alpha r^2}$$
$$\chi^{STO} = \sum_v k_v \chi_v^{GTO}$$

- An example of an STO and how it can be approximated with one or more GTO's. One GTO only is not very good, but 4 GTO's already are quite close.



- The most popular basis function sets $\{\chi\}$ are the Gaussian functions developed by the group of J. A. Pople (Nobel prize in chemistry 1998). These sets of functions can be divided as follows:

  - In the so called **minimal basis set** there is one orbital for two core electron orbitals, and one orbital for each valence electron. Every STO is replaced by a sum of N GTO-functions (STO-nG). The most common minimal set is the STO-3G set.

- To improve on the results the basic approach is to increase the size of the basis sets. In the so called “Double Zeta” set there are twice as many orbitals as in the minimal set. If the doubling is made only with valence electrons (which are usually the most interesting ones) one obtains the “Split Valence” set of basis functions.

- In the so called 3-21G set the first row elements have 3 GTO’s for 1s electrons, 2 GTO’s for 2s, 2p and so forth electrons, and the extra valence electrons are described by one GTO. This set is quite popular nowadays.

- Other even larger basis sets: 6-31G, sets which have polarization functions, etc. etc.

Limitations of the basic Hartree-Fock method

- The method does not at all account for electron correlation, that is, the correlation between the momentaneous motion between electrons. This energy is usually only of the order of 1 % of the total, but can sometimes be comparable to the total binding energy of the system and hence quite significant. Several methods have been developed to take this into account:

  - In the Configuration Interaction (CI) method a linear combination out of Slater determinants is formed. This is a very good approach, but unfortunately also very slow.

  - In Møller-Plesset perturbation theory a perturbation series is made out of the error in the correlation energy. The most popular approach is MP2, which takes into account the lowest-order correction.

  - In Multiconfiguration SCF (MCSCF) a small CI term is included in the HF iteration.

Density functional theory

- Density functional theory, DFT, is in addition to the HF methods the most widely spread method to calculate electronic structure in materials. Because it is computationally more efficient than HF, it has become especially popular among solid state physicists who need many atoms to describe a solid.

- As in the HF methods, the approach starts with the Schrödinger equation for electrons

$$\left\{-\sum_{i=1}^{I}\frac{h^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_{i=1}^{I}\sum_{j=1}^{I}\frac{e^2}{|\mathbf{r}_{ij}|^2} + V_{ne}\right\}\psi(n, \mathbf{r}) = E_e(n)\psi(n, \mathbf{r})$$

  or

$$\sum_i (T_e + V_{ee} + V_{ext})\psi = E\psi$$

  where V_{ext} is the so called external potential acting on the electrons due to the nuclei.

- DFT is based on the Hohenberg-Kohn theorems [Hohenberg and Kohn, Phys. Rev. **136** (1964) 864]:

  Theorem I: For any given set of electrons which are in an external potential V_{ext}, this potential is determined uniquely, except for a trivial additive constant, from the electron density $n(\mathbf{r})$.

  Corollary I: Because the system Hamiltonian is thus fully determined short of an energy shift, the electron density can be used to fully derive the many-particle wave function and thus all desired system properties.

  Theorem II: It is possible to define a universal *functional* for the energy $E[n]$ depending on the electron density $n(\mathbf{r})$. The true ground state energy is the global minimum of the energy functional, and the density $n(\mathbf{r})$ which minimizes the functional is the exact ground state density.

  Corollary II: The functional $E[n]$ is enough to determine the true ground state energy and electron density. Excited states must be determined otherwise.

Kohn-Sham ansatz

[W. Kohn and L. J. Sham, Phys Rev. **140** (1965) 1133]
[parts from http://www.fysik.dtu.dk/~bligaard/ms/node11.html]

(W. Kohn obtained the Nobel prize in chemistry in 1998 essentially for the Hohenberg-Kohn theorem and the Kohn-Sham ansatz, sharing the prize with J. A. Pople)

The idea of the *ansatz* is that the original, complicated Hamiltonian can be replaced by another Hamiltonian function which is easier to solve. This effective Hamiltonian H_{eff} describes *non-interacting "electrons"* in a system which is *assumed* to have the same density as the true system with interacting electrons. The orbitals of the non-interacting electrons are called Kohn-Sham orbitals.

- When the Hohenberg-Kohn variational principle is applied to the Kohn-Sham orbitals, the following canonical Kohn-Sham orbital equations are obtained:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

where i runs over all electrons, ε_i is the Kohn-Sham eigenvalue of electron i, and the effective one-particle potential is:

$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \phi_{\mathrm{e}}(\mathbf{r}) + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$$

Here V_{ext} is the external potential and

$$\phi_{\mathrm{e}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

So we now have an equation for the non-interacting Kohn-Sham orbitals which is formally a Schrödinger equation.

$$-\frac{1}{2}\nabla^2\psi_i(\mathbf{r}) + V_{\mathrm{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

and the electron density is

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

If the exchange-correlation energy is known, these equations can be solved with a similar self-consistent iteration process as the Hartree-Fock equations, which should give a realistic total electron density.

Note, however, that the Kohn-Sham orbitals and their eigenvalues ε_i do not have a clear physical interpretation. There is no guarantee that they have any relation to real electron energies and wave functions, but it appears that they are in fact a surprisingly good approximation of the real electron properties.

Local density approximation (LDA)

- So far the DFT approach has not made any approximations, only assumptions. But the to obtain the exchange-correlation functional $E_{\mathrm{xc}}[n]$ some approximation is needed. The most used one is the **local density approximation, LDA:**

$$E_{\mathrm{xc}}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r})) \quad ,$$

  where $\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))$ is the exchange and correlation energy of a homogeneous electron gas per one electron. So, in every density element in space the electron density is assumed to be constant, and the energies associated with these are summed up.

- The exchange functional can be as simple as (Dirac LDA)

$$E_{x,\,Dirac}^{LDA} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int n(\boldsymbol{r})^{4/3} d\boldsymbol{r}$$

- Once an exchange and correlation energy for a homogeneous gas is introduced (several exist), the equations can be solved with an iteration process:

    1) Start with some $V_{\text{eff}}(\mathbf{r})$.
    2) Calculate the one-electron wave functions ψ_i and from these the density $n(\mathbf{r})$
    3) Using the new $n(\mathbf{r})$ calculate a new $V_{\text{eff}}(\mathbf{r})$.
    4) Repeat steps 2 and 3 until we have obtained a self-consistent (non-changing) solution.

- It is also possible to account for the spin in the exchange and correlation term, in which case the term **local spin density approximation, LSDA** is used.

- When the results of density functional theory is compared to experimental data and other methods, at least the following limitations of DFT - LDA have been found:

    1) They generally predict too large cohesive energies for solids
    2) Too large total energies for atoms

    3) Too small energy gaps for many semiconductors (LDA actually predicts that the gap in Ge is 0, that is, that Ge is a metal !).
    4) The method is unstable for negative ions and gives a too diffuse electron density

- To improve on the accuracy of DFT people have introduced exchange-and-correlation functionals which also depend on the variation of the electron density:

$$E_{\text{xc}}[n(\mathbf{r}), dn(\mathbf{r})]$$

  There are numerous of these so called Generalized Gradient Approximations (GGA). I will here only give the following citation describing on how they are selected [http://www.fysik.dtu.dk/~bligaard/ms/node16.html:

"The development of gradient corrections, which actually improves on the local functionals, has been following two different ideas. The idea primarily advocated by Becke is that "everything is legal". *The argument here is that going away from the local density functionals, the true first principles or ab initio aspect is generally lost.* One can therefore choose any functional for any reason, and the quality of the functional is then determined afterwards by actual application to physical systems. The idea of Becke stands in contrast to the idea primarily advocated by Perdew that the development of exchange-correlation functionals should be based on basic principles derived from quantum mechanics. These basic principles can be scaling relations, correct limits for high and low densities, correct LSDA limit for slowly varying densities as well as fulfilment of exact relations on the exchange and correlation holes.

The very pragmatic way of Becke has been and still is the preferred way to develop functionals for use in quantum chemistry (here implying applications to isolated atoms and molecules)."

- So in practice there are a large number of GGA's around, and people choose one which for some reason has been found to work well in their system.

Plane-wave methods and pseudopotentials

- To describe solids, so called Plane-Wave methods are very popular. In these the basic algorithms are as in DFT. But now tightly bound core electrons and the outer valence electrons are described separately. The outer valence electrons are described as a sum of plane waves:

$$\psi = \sum_{l}^{N_l} f_l(\boldsymbol{K}_l) e^{-i\boldsymbol{K}_l \cdot \boldsymbol{r}}$$

  where the wave vectors $\boldsymbol{K}_l$ are chosen to that they have the same periodicity as the simulation cell. Because of the basic mathematics of Fourier series, it is clear that any shape of the electron wave functions can in principle be described with this sum provided the sum has enough terms N_l. Using these functions also has the advantage that the very well developed and efficient Fast Fourier transform (FFT) method can be used in the solution.

  But usually the inner (core) electrons of the atoms are describes with spherically symmetric wave functions

$$\phi \sim \sum_{lm} R_l(r) Y_{lm}(\theta, \varphi)$$

  which are centered at each nucleus, and constructed such that these match the plane wave functions at some radius from the nucleus. The inner electron functions are called the **pseudopotential** and the radius the **pseudopotential radius.**

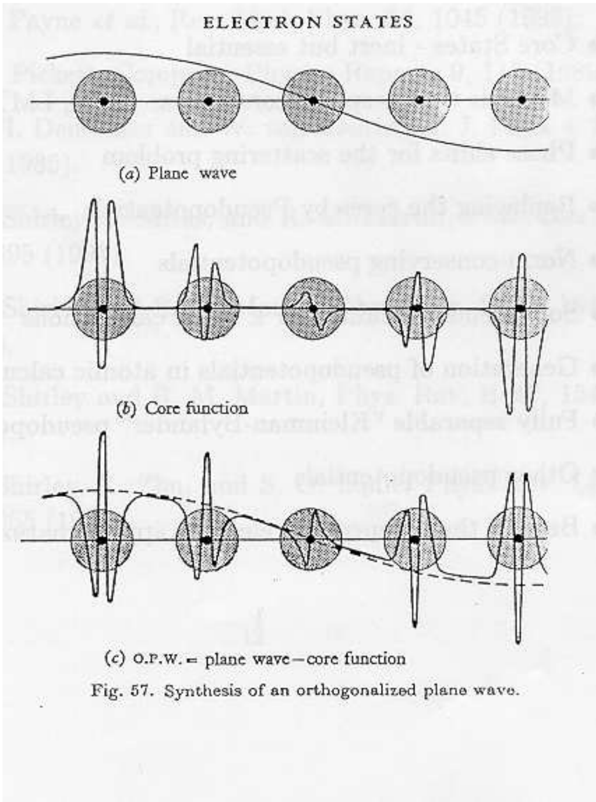


Fig. 57. Synthesis of an orthogonalized plane wave.

The introduction of pseudopotentials is computationally very favourable, since a large number of terms N_l would be needed to describe the strongly varying core electron wave functions.

Names of some common plane wave methods:

- APW = Augmented Plane Wave
- LAPW = Linear APW
- FLAPW = Fully LAPW
- SAPW = Spline APW
- OPW = Orthogonal Plane Wave

etc. etc.

- The counterpart to pseudopotential methods are the **all electron methods.**

- The main measure of the accuracy of plane-wave methods is the number of plane waves used to describe the system. The more points, the more accurate and slower the simulation is (similar to the number of basis functions in atomic calculation).

Examples of results of DFT / plane-wave calculation results:

Atomization energies of molecules (eV).

Molecule	HF	LSD	PW91	Expt.
C_2 [a]	0.73	7.51	6.55	6.36
C_6H_6 [a]	45.19	68.42	61.34	59.67
H_2 [b]	3.29	4.65	4.52	4.49
H_2O [b]	5.71	11.00	9.59	9.51
O_2 [b]	1.25	7.48	5.93	5.12

[a] From [19], using a basis set of 18 *s*-type, nine *p*-type, and four *d*-type single Gaussians on each atom. For C_2 and C_6H_6, the zero-point vibrational energy has been omitted from the calculated and experimental values.
[b] PW91, using a triple-zeta valence plus polarization basis set, and Expt. are from [38]; HF, using a 6-31G* basis, from [28]; and LSD, using a basis-free numerical method, from [23].

Results for the lattice constant a and bulk modulus B for C and Si:

Examples of Results - Diamond Structure

	Carbon		Silicon	
	a (A)	B (Mb)	a (A)	B(Mb)
Experiment	3.56	4.42	5.43	0.99
Ab Initio Pseudopotential				
Yin, Cohen, 1980-2	3.60	4.33	5.45	0.98
Biswas, et. al., 1984	3.54	4.94	--	--
Nielsen, Martin, 1983	--	--	5.40	0.93
LMTO				
Glotzel, Segall, Andersen, 1980	3.53	4.90	5.41	0.98
McMahan, 1984	3.55	4.64	5.45	0.95
LCAO				
Harmon, Weber, Hamann, 1982	--	--	5.48	0.87

So it is quite possible to obtain the quantities to an accuracy ~ 1 %.

Car-Parrinello MD

- The Car Parrinello method [R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985)] is a method where the electron and atom motion is updated at the same time. The method has become very popular because it is highly efficient and can also be parallelized well.

  (in Finland the FINGER (FINnish General Energy Relaxator) code, developed in Risto Nieminens group, is an efficient Car-Parrinello code which enables dynamic DFT simulations in ~ 200 atom systems in the Finnish Cray T3E).

Commercial HF and DFT programs

- In practice, a large fraction of modern HF, DFT- and empirical simulations are carried out with commercial codes.

  A large fraction of the most popular codes are available at the CSC (Center for Scientific Computing) computers, which can be used by any University research group for free.

  In commercial codes, the algorithms are typically 5-15 years or old. This is a mixed blessing: the state-of-the art methods may not be available, but on the other hand the algorithms in there are usually well tested. Roughly speaking especially the methods favoured by chemists have moved over to commercial codes, whereas physicists tend to stick to their own or non-commercial codes.

  The commercial codes have flashy and easy-to-use graphical user interfaces. This is good in one sense, but also makes the risk to do **Garbage in - Garbage out**-kinds of simulations very large. So don’t blindly start using a commercial code, you should understand its inner workings and the physics in there first!

- examples of HF-codes:
  - Gaussian — The code deriving from Poples work. Very popular and versatile code. Nowadays also a DFT version is part of the package.
  - TurboMole
- DFT-codes
  - CASTEP — A plane-wave DFT code
  - DMol^3 — DFT code based on numerical basis sets, rather than Gaussian Sets
  - VASP — A semi-commercial DFT code developed in Vienna
- Other important stuff
  - InsightII — The graphical user interface of Molecular Simulations Inc:in (MSI), from which most MSI and some non-commercial codes such as DMol- and Gaussian can be run.
  - Cerius2 — Another MSI user interface, can run many of the same codes as InsightII

Tight-binding methods

[Main source: Foulkes *et al.*, Phys. Rev. B **39** (1989) 12520]

- Tight-binding models can be considered "minimal" quantum mechanical models. They are most often semi-empirical, and the quality of the results varies a lot. At best, one can achieve results comparable to DFT with a 100 times less computer capacity, at worst they are no better or even worse than semi-empirical models but a 100 times slower!

- In semi-empirical TB one starts with the *assumption* that total electronic energy E can be written as

$$E = \sum_{i=1}^{N} \varepsilon_i + \frac{1}{2}\sum_i \sum_j U(r_{ij})$$

  where U is a repulsive classical pair potential acting between the atoms, and the ε_i are eigenvalues of some self-consists Schrödinger-like equation,

$$\hat{H}\psi_i(r) = \left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi_i(r) = \varepsilon_i(r)$$

  This resembles the DFT formalism, and can be derived with various approximations.

- The eigenvalues ε_i are negative, and the repulsive energy positive. U(r) is either constructed by empirical fitting to give the desired total energy, or derived from DFT.

The TB Schrödinger is solved with the variational principle for some set of basis functions $\{\phi_\alpha\}$ which leads to a secular equation

$$|H - \varepsilon S| = 0$$

where

$$H_{\alpha\beta} = \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle$$

and

$$S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$$

Often one still assumes that the set of basis functions is orthogonal, in which case *S* reduces to the unit matrix.

Usually the basis set is put to contain only the outermost electrons, with all others treated with the repulsive potential U(r). The elements in the basis function set are usually also fit to experimental data.

For instance, to treat a material where only the outer s and p electrons are important, one can get away with using only for basis functions (ssσ, spσ, ppσ and ppπ). If one want to also describe d electrons, one needs at least 10 basis functions.

Roughly speaking it seems that TB methods usually works well in materials with only covalent bonding. Systems where much work has been done and which have been found to work well are at least C, Si and their hydrogen compounds.

An example of a O(N) TBMD application

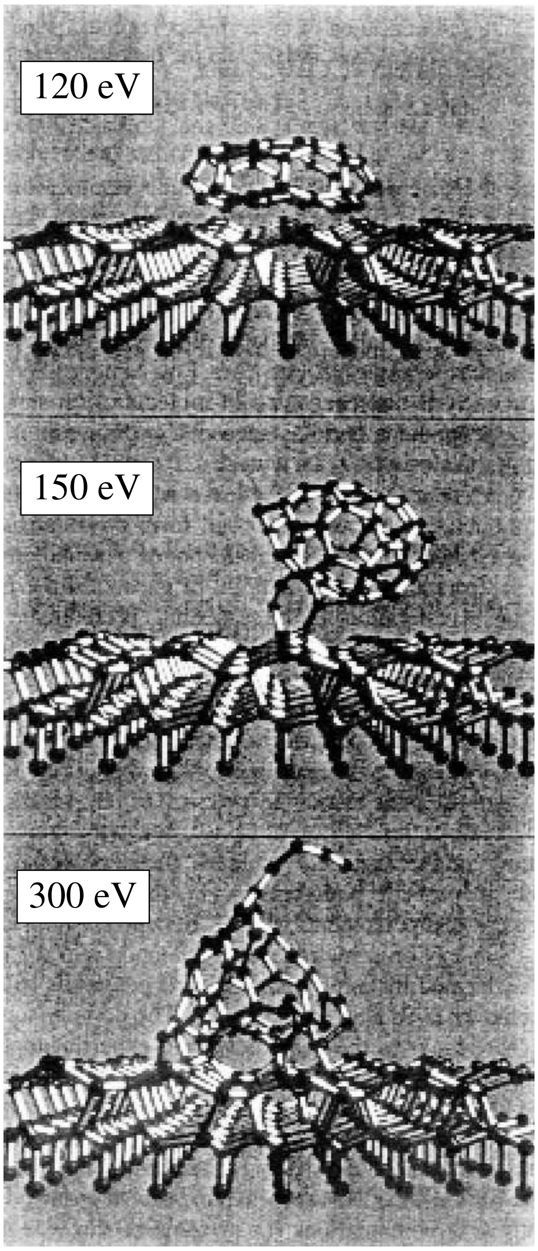
[G. Galli and F. Mauri, Phys. Rev. Lett. 73 (1994) 3471]

- A fullerene C_{60} colliding with a diamond surface with different kinetic energies E_k (the surface is a reconstructed (111) surface with no dangling bonds):

-When $E_k \leq 120$ eV no bonds are formed between the fullerene and the surface, and the fullerene simply bounces off it.

- When 120 eV < E_k <240 eV a few bonds are formed between the fullerene and the surface, and the fullerene may stick to the surface. The bonds may also be quickly broken again and the fullerene can bounce off again.

- When $E_k \geq 240$ eV several bonds are formed between the fullerene and the surface, the fullerene breaks down almost completely, and sticks to the surface.



Very brief mention of a few other methods

Quantum Monte Carlo

- Quantum Monte Carlo (QMC) are a set of DFT-related methods where Monte Carlo simulation techniques are used to minimize the correlation term of DFT. These are computationally very expensive, but they can give very accurate results, especially for the correlation term which is difficult to treat otherwise.The most common varieties or Diffusion Monte Carlo (DMC) and Variational Monte Carlo (VMC)

- Just an example on results [Grossman *et al.,* Phys. Rev. Lett. **75** (1995) 3870]:

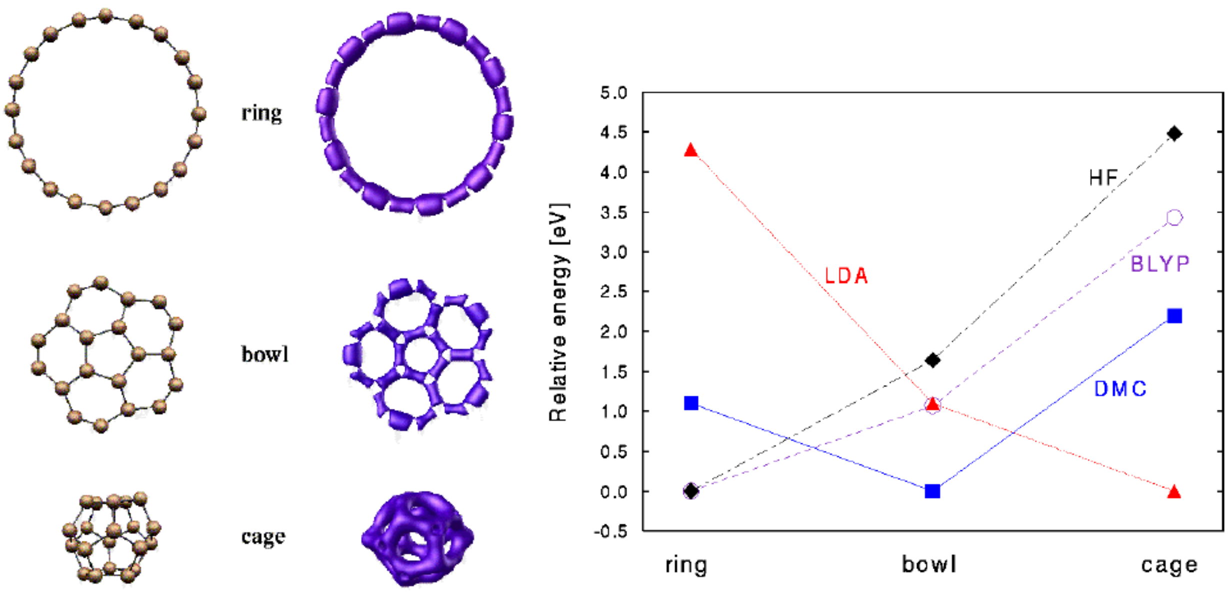
TABLE I. Binding energies [eV] of small hydrocarbons calculated using the HF, LDA and DMC methods. Experimental values are listed for comparison.

	HF	LDA	DMC	Exp.
methane (CH_4)	14.20	20.59	18.28(5)	18.19
acytylene (C_2H_2)	12.70	20.49	17.53(5)	17.59
ethylene (C_2H_4)	18.54	28.19	24.44(5)	24.41
ethane (C_2H_6)	23.87	35.37	31.10(5)	30.85
allene (C_3H_4)	22.63	35.87	30.36(5)	30.36
propyne (C_3H_4)	22.70	35.70	30.55(5)	30.45
benzene (C_6H_6)	44.44	70.01	59.2(1)	59.24

1. A comparison of methods:

=> DMC gives all energies correct within the uncertainties, and clearly outshines HF and plain LDA.

2. What is the minimum-energy configuration of C_{20} ?



=> According to QMC:n it is) the “bowl” shape

=> Note the large differences between the supposedly reliable DFT and HF methods, and that none of the agrees with the QMC behaviour.

Path Integral Molecular Dynamics

- Path Integral MD (PIMD) is a DFT / Car-Parrinello type of method which uses a Feynman path integral representation of the density matrix.

  Also hideously expensive computationally, but claimed to be the only really good method to describe water-related reactions.

- A rough rule of thumb for both QMC and PIMD is that the number of atoms is limited to ~ 20 or so...

Time-dependent HF, DFT, TB

- The methods described until now are all normally used to obtain the ground state. This means one assumes that the electron system has time to come to rest before the processes of interest happen. Since electronic relaxation times are typically of the order of femtoseconds, this is often a very good approximation.

- However, if one is interested in e.g. electronic excitation, this approximation is not valid, and one has to actually solve the time-dependent Schrödinger equation. This can be done by iterating over time

- Time-dependent (TD)-methods are somewhat of a hot topic in electronic structure calculations now, and there are TD variations of all the main methods: HF, DFT and TB.

- A rough rule of thumb is that a TD-method is at least a factor of 100 slower than the corresponding ordinary method.