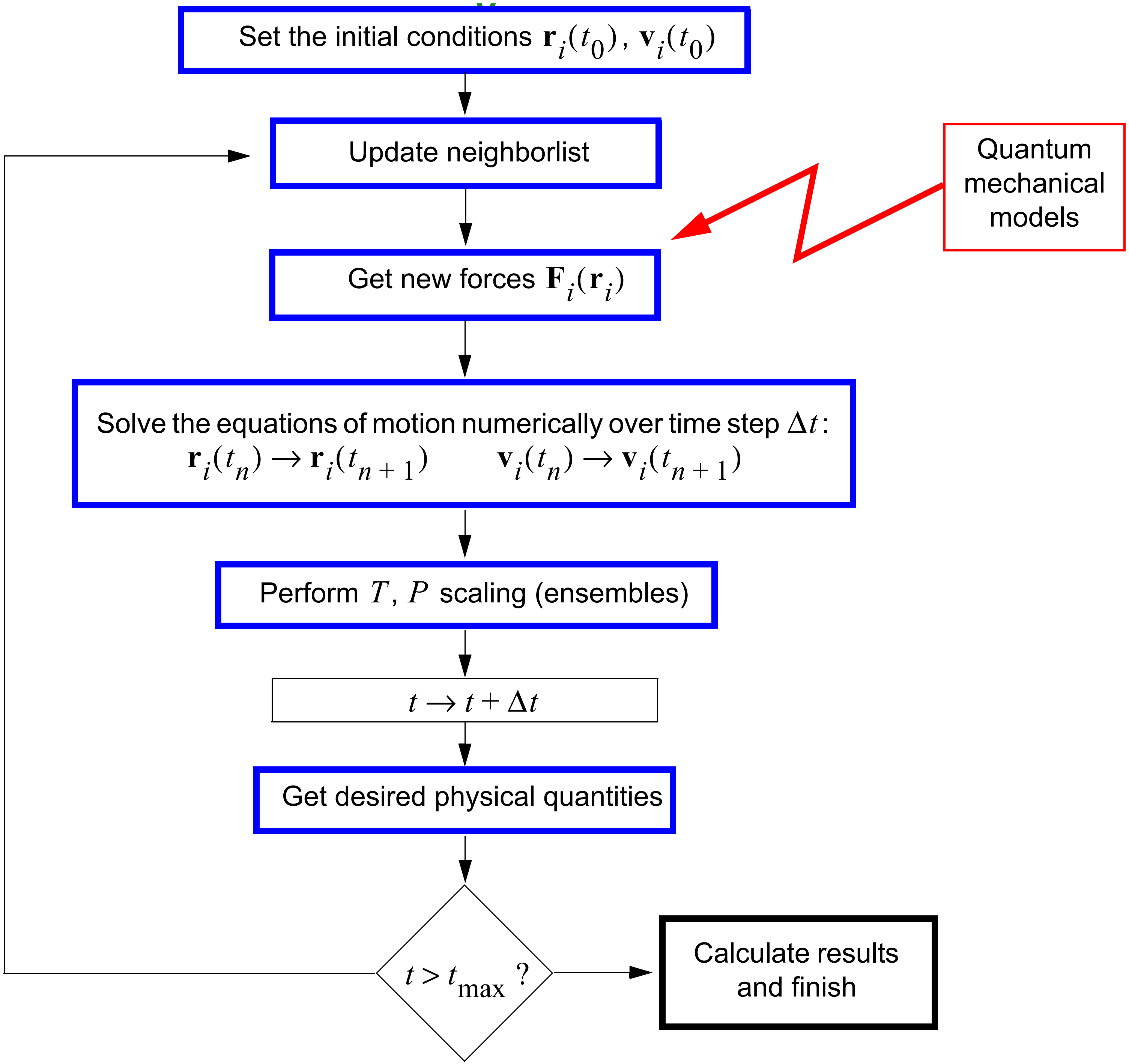


Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Quantum mechanical models

Solve the equations of motion numerically over time step Δt:

$$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

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.
  - Assumes: interactions between the nucleons neglected
  - This is also assuming relativistic effects can be ignored
  - Time-dependent Schrödinger equation: dynamics without MD alogrithm

Almost always true

Not always true for heavy elements

- But solving the full equation is extremely expensive computationally, and hence one always has to resort to various levels of approximation
- Term “***ab initio***” or “***first principles***” much used in this context to mean methods ***with no empirical input***
  - But may have several, even dubious, approximations!
  - semi-empirical= some empirical input used in choice of parameters or model

Model	Type	Scaling	$N_{\max}$
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, not always *ab initio*	$O(N^3)$ $O(N)$	1000
TB (Tight-binding)	quantum mechanical (often semiempirical)	$O(N^3)$ $O(N)$	1000 10000
MBP (Many-body potential)	classical, semiempirical	$O(N)$	10^8
PP (Pair potential)	classical, semiempirical	$O(N)$	10^9

Atomistic interaction models

- $O(N)$ variants of all classes of methods
  - The quantum mechanical $O(N)$ methods new $\Rightarrow$ work (so far) well only in a limited set of problems

- 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:

$$\begin{aligned} A_{\text{MBP}} &= 3 \times A_{\text{PP}} \\ A_{\text{TB}} &= 100 \times A_{\text{MBP}} \\ A_{\text{DF or HF}} &= 100 \times A_{\text{TB}} \end{aligned}$$

- Quantum mechanical models (HF and DFT): ~ 100 atoms $\Rightarrow$ e.g. small molecules, bulk properties of common phases, and point defect properties.

- TB, a ***minimal quantum mechanical*** model works well in a few materials (e.g. C, Si, Ge) but is problematic in many others.

- Classical models: possible to simulate very large systems, such as large protein molecules, 2- and 3-dimensional defects, whole nanoclusters, surface growth, grain boundaries etc.
  - No information on the electronic properties of the material.

Atomistic interaction models

- This chapter is a short overview on the methods; more information on other, specialized courses on the subject
  - ***A huge topic in itself! Mainly outside the scope of this course***

- Literature:
  - R. Phillips: *Crystals, Defects and Microstructures*, (Cambridge University Press, 2001), Chapter 4
  - A. Sutton: *Electronic Structure of Materials*, (Oxford Science Publications, 1996)
  - M. Finnis: *Interatomic Forces in Condensed Matter*, (Oxford Series in Materials Modelling, 2003)
  - R. M. Martin: *Electronic Structure: Basic Theory and Practical Methods*, (Cambridge University Press, 2004)

- There is a large number of review articles. A good one for those who do DFT calculations but are not quite experts in the field is

  Designing meaningful density functional theory calculations in materials science—a primer
  Ann E Mattsson et al. *Modelling Simul. Mater. Sci. Eng.* **13** (2005) R1-R31.

Overview of quantum mechanical models

- A system of N nuclei and I electrons with coordinates $\mathbf{r}_n$ $(n = 1\ldots N)$ and $\mathbf{r}_i$ $(i = 1\ldots I)$:
- **Schrödinger equation**

$$H\Psi = E\Psi$$

  - Hamiltonian operator H

$$H = -\sum_{n=1}^{N}\frac{\hbar^2}{2M_n}\frac{\partial^2}{\partial\mathbf{r}_n^2} - \sum_{i=1}^{I}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}_i^2} + \frac{1}{2}\sum_{i=1}^{I}\sum_{j=1}^{I}\frac{e^2}{|\mathbf{r}_{ij}|} \qquad (7.1)$$

$$+ \sum_{n=1}^{N}\sum_{i=1}^{I}\frac{Z_n e^2}{|\mathbf{r}_{ni}|} + \frac{1}{2}\sum_{l=1}^{N}\sum_{n=1}^{N}\frac{Z_n Z_l e^2}{|\mathbf{r}_{nl}|}$$

$$= T_\mathrm{n} + T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne} + V_\mathrm{nn}$$

  - Here:
    - T_n and T_e are the kinetic energies of the nuclei and electrons, respectively.
    - V_ee, V_ne and V_nn are the electron-electron, electron-nucleus and nucleus-nucleus Coulomb interactions ⇒ Schrödinger equation.
      $(T_\mathrm{n} + T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne} + V_\mathrm{nn})\Psi = E\Psi$ (7.2)
    - Ψ is the total wavefunction of the full nucleus-electron system.

Born-Oppenheimer approximation

- For any given configuration of the nuclei one can assume that the electrons find their ground state before the atoms move significantly.
  - Classical simulations also based on the Born-Oppenheimer approximation: interatomic potentials do not depend on the atom motion.

- Mathematically: the wavefunction Ψ is separated into a product

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

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

  - $\psi(n, \mathbf{r}_i)$ fulfills the wave equation

$$\{T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{ne}\}\psi(n, \mathbf{r}) = E_\mathrm{e}(n)\psi(n, \mathbf{r}) \qquad (7.3)$$

where V_ne is the nucleus-electron potential of the original Hamilton operator.

  - Solution of this gives the electronic total energy of the system as a function of the positions of the nuclei.
    - Can also be used to give the forces acting between atoms ⇒ atom motion can be simulated using the classical MD algorithm (*ab initio* MD)

Hartree-Fock methods

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

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

- The basic solution in **Hartree-Fock** (as well as in DFT) is to create some sort of ***average*** **electron density** with which every electron interacts independently:

$$V'_{\mathrm{ee}} = \sum_i V_i^{\mathrm{av}}$$

- Pauli exclusion principle: a Slater determinant of one-electron wave functions

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

Hartree-Fock methods

- 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.**

- Thus the new central problem becomes to find a good form for the average potential V_i^{av}.
  - Iteration: initial guess for the wave functions ϕ_i, plugged 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 **self-consistent field** has been found (HF-SCF).

- The eigenvalues of the energy have a clear physical interpretation: ionization energy of the electron

- The SCF method fulfills the variational principle:
  - The eigenvalue 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.

Hartree-Fock methods

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

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

  - In the most straightforward approach the **basis functions** χ_{μ} can be so called Slater type orbitals (**STO**)

$$\chi = R(r)Y_{lm}(\theta, \phi), \begin{cases} R_{1s} = N_1 e^{-\zeta r} \\ R_{2s} = R_{2p} = N_2 r e^{-\zeta r} \end{cases}$$

  which somewhat resemble orbitals of the hydrogen atom:

$$\psi_{nlm}(r, \theta, \phi) \propto e^{-\alpha r/2}(\alpha r)^l L_{n-l-1}^{2l+1}(\alpha r) Y_l^m(\theta, \phi), \quad \alpha = 2Z/na_0, \quad a_0 = \hbar^2/me^2.$$

  - Integrating these STO orbitals is numerically difficult, however.

Hartree-Fock methods

- Computationally it is much more favourable to use Gaussian-type orbitals **(GTO)**

$$\chi^{\mathrm{GTO}}(r) = e^{-\alpha r^2}$$

because a product of two Gaussians is a Gaussian:

$$e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} e^{-\beta|\mathbf{r}-\mathbf{R}_B|^2} = K_{AB} e^{-\gamma|\mathbf{r}-\mathbf{R}_C|^2},$$

$$\gamma = \alpha + \beta,$$

$$\mathbf{R}_C = \frac{\alpha \mathbf{R}_A + \beta \mathbf{R}_B}{\alpha + \beta},$$

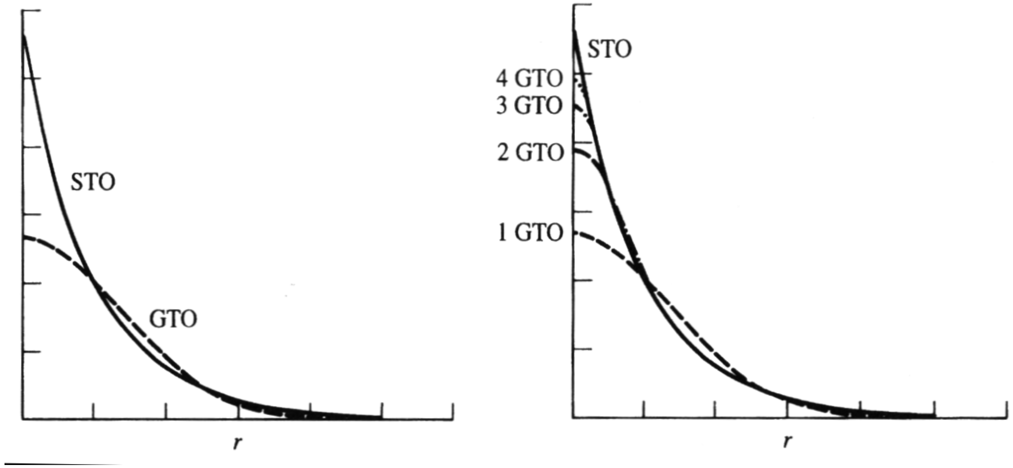
$$K_{AB} = \left[\frac{2\alpha\beta}{\pi(\alpha+\beta)}\right]^{3/4} e^{-\frac{\alpha\beta}{\gamma}|\mathbf{R}_A - \mathbf{R}_B|^2}$$

- But real electron wave functions are not Gaussian in shape ⇒ use a sum of GTO’s to describe the wave function:

$$\chi^{\mathrm{STO}} = \sum_v k_v \chi_v^{\mathrm{GTO}}$$

Hartree-Fock methods

- 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.



A.R.Leach, Molecular Modelling

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

Hartree-Fock methods

- 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 one of 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.
- Starts with the Schrödinger equation for electrons

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

or

$$\sum_i (T_{\mathrm{e}}+V_{\mathrm{ee}}+V_{\mathrm{ext}})\Psi = E\Psi$$

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

- The basic idea of DFT: instead of manybody wavefunction $\Psi(\{\mathbf{r}_i\})$ use electron density $n(\mathbf{r})$
  - Only need to calculate a scalar function of one vector variable not I vectors

Density functional theory

- DFT is based on the Hohenberg-Kohn theorems [Hohenberg and Kohn, *Phys. Rev.* 136 (1964) B864]:

  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 by other means.

Density functional theory

- **Kohn-Sham ansatz** [W. Kohn and L. J. Sham, *Phys Rev.* **140** (1965) A1133]

  [see http://www.fysik.dtu.dk/~bligaard/wwwdirectory/phdthesis/phdproject.pdf]

  - 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 describes *non-interacting "electrons"* in a system which is *assumed* to have the same density as the true system with interacting electrons.
  - To put it in another way: We assume that there exists a system of non-interacting electrons that produce the same electron density $n(\mathbf{r})$.

  - The orbitals $\psi_i(\mathbf{r})$ of the non-interacting electrons are called Kohn-Sham orbitals.

- Apply Hohenberg-Kohn variational principle to the Kohn-Sham orbitals ⇒ the Kohn-Sham orbital equations

$$E[n] = T_0[n] + \frac{1}{2}\iint\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}' + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E_{\mathrm{xc}}[n],$$

Note that the *Hartree atomic units* are used here: $e = m = \hbar = 4\pi\varepsilon_0 = 1$

where $T_0[n]$ in now the kinetic energy of *non-interacting* electrons.

  - All the problematic terms are collected under $E_{\mathrm{xc}}[n]$:

    error in the kinetic energy: $T[n] - T_0[n]$

    error in the Coulomb interaction between electrons: $E_{ee} - \frac{1}{2}\iint\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}'$

    correlation and exchange energies (quantum mechanical effects).

Density functional theory

- What we have gained here is that the above terms in E_{xc} are (usually) small corrections and can be calculated in an approximative way.

- The variational principle gives then

$$\frac{\delta E[n]}{\delta n} = 0 \Rightarrow \left(-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

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

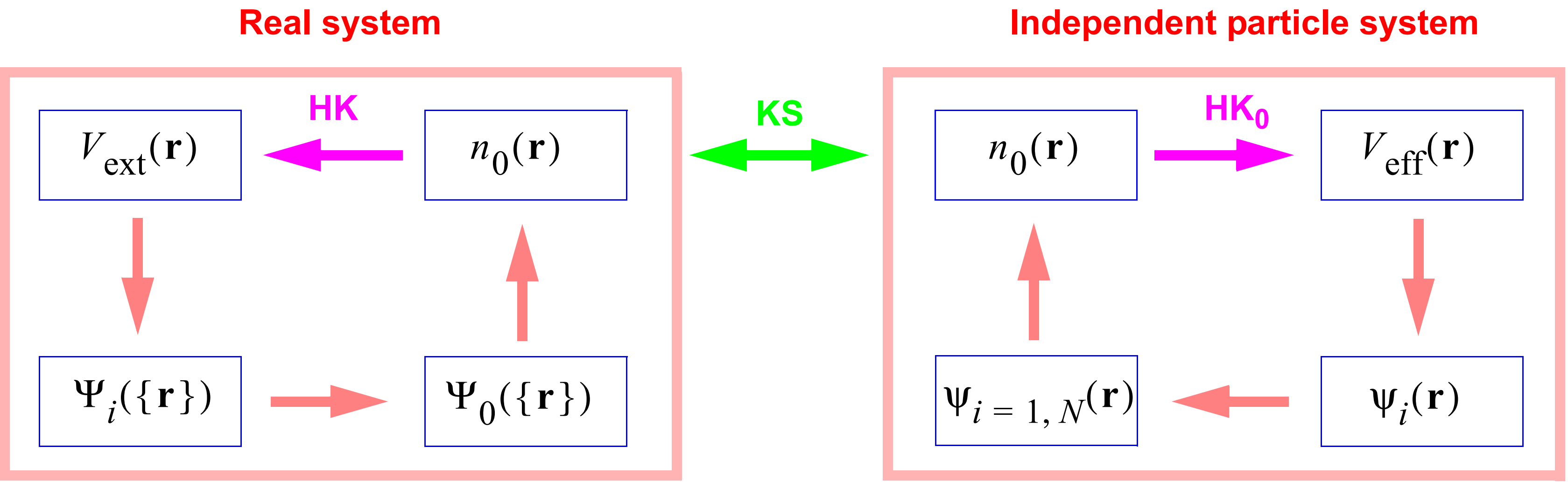
$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \phi_{\mathrm{e}}(\mathbf{r}) + \frac{\delta E_{\mathrm{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

- Here V_{ext} is the external potential and

$$\phi_{\mathrm{e}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

Density functional theory

- Pictorially this can be presented as[1]



Real system

Independent particle system

$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d] & n_0(\mathbf{r}) \arrow[l, "\text{HK}"'] \arrow[r, leftrightarrow, "\text{KS}"] & n_0(\mathbf{r}) \arrow[r, "\text{HK}_0"] & V_{\text{eff}}(\mathbf{r}) \arrow[d] \\
\Psi_i(\{\mathbf{r}\}) \arrow[r] & \Psi_0(\{\mathbf{r}\}) \arrow[u] & \psi_{i=1,N}(\mathbf{r}) \arrow[u] & \psi_i(\mathbf{r}) \arrow[l]
\end{tikzcd}$$

---

1. Adapted from R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, (Cambridge University Press, 2004), Fig. 7.1

Density functional theory

- If the exchange-correlation energy is known, these equations can be solved by self-consistent iteration
  - 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.
    - To obtain the exchange-correlation functional $E_{\mathrm{xc}}[n]$ the **local density approximation, (LDA)** is used:

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

where $\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))$ is the exchange and correlation energy of a **homogeneous electron gas** per one electron.

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

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

Density functional theory

- 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 $V_{\mathrm{eff}}(\mathbf{r})$.
  2) Calculate the one-electron wave functions $\psi_i \Rightarrow$ new density $n(\mathbf{r})$
  3) New $n(\mathbf{r}) \Rightarrow$ new $V_{\mathrm{eff}}(\mathbf{r})$.
  4) Repeat steps 2 and 3 until we have obtained a self-consistent solution.

- Spin in the exchange and correlation term: **local spin density approximation, LSDA**.
- DFT-LDA results compared with experimental data:
  1) Generally too large cohesive energies for solids
  2) Too large total energies for atoms
  3) Too small energy gaps for many semiconductors (LDA actually predicts zero gap for Ge!).
  4) 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:

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

  - There are numerous of these so called Generalized Gradient Approximations (GGA).
    - 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. This gives a semi-empirical character to the methods, i.e. they are not pure *ab initio*
- The DFT solution method does not restrict the way we express the Kohn-Sham wave functions.
  - Below are given two nowadays common ways to build the **basis sets** used in DFT calculations: plane waves and atomic-type orbitals.

Plane-wave methods

- In plane-wave methods the basic algorithms are as in DFT but:

Search for wave functions → search for coefficients

- The outer valence electrons are described as a sum of plane waves:

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

where the wave vectors $\mathbf{K}_l$ are chosen to that they have the same periodicity as the simulation cell.

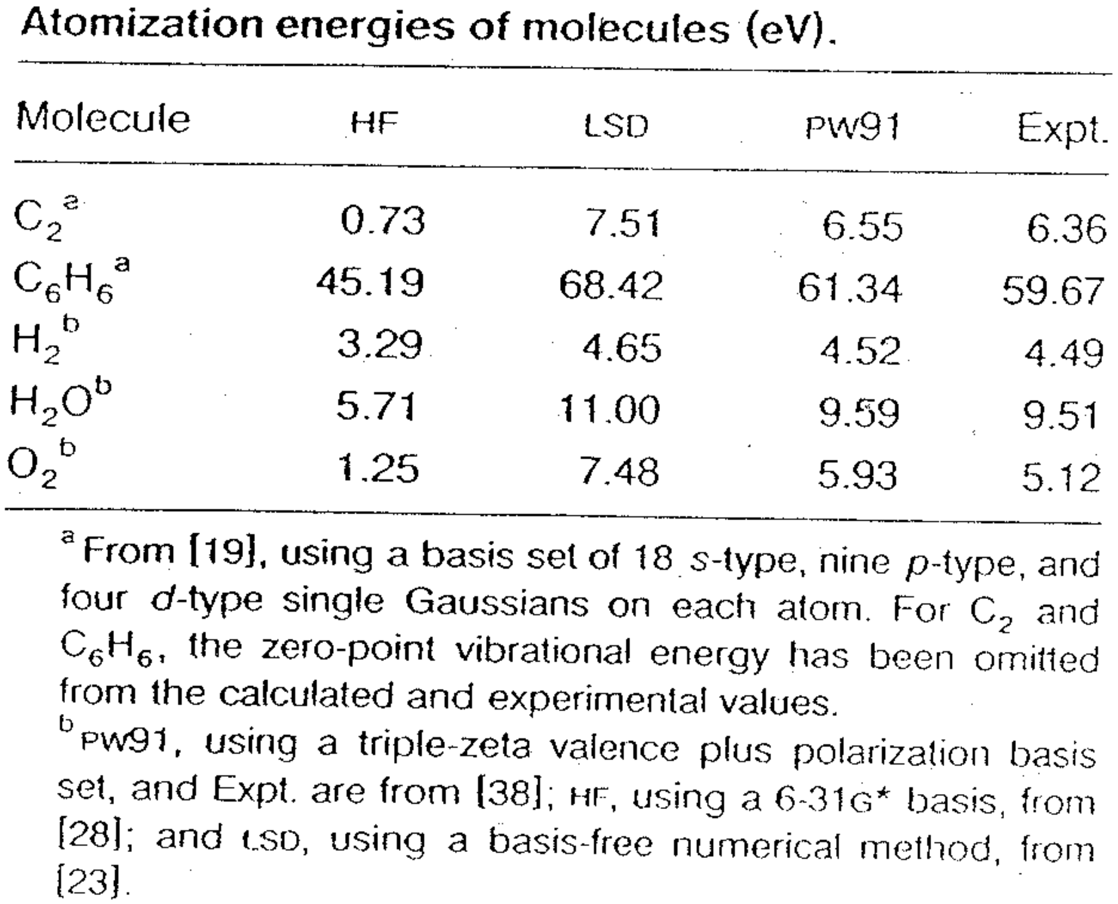
- Any shape of the electron wave functions can in principle be described with this sum provided ***the sum has enough terms*** N_l.

- Names of some common plane wave methods:
  - APW = Augmented Plane Wave
  - LAPW = Linear APW
  - FLAPW = Fully LAPW
  - SAPW = Spline APW
  - OPW = Orthogonal Plane Wave

- The main measure of the accuracy of plane-wave methods is the number of plane waves used to describe the system.

Plane-wave methods

- 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].

LCAO methods

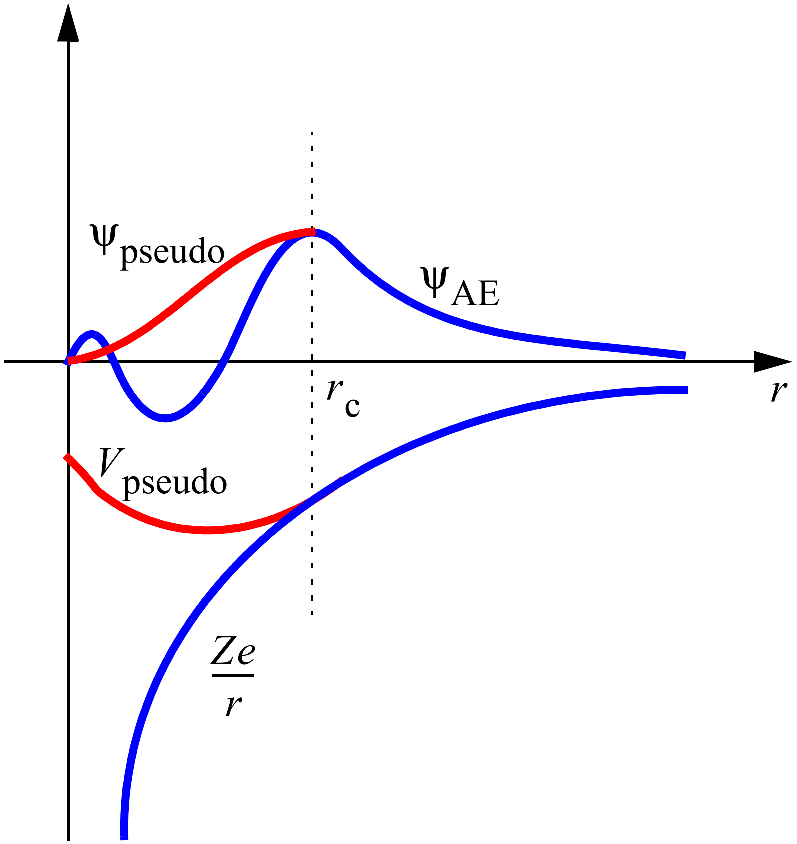
- In the **LCAO** (Linear Combination of Atomic Orbitals) method the basis set consists of orbitals **localized around each atom** in the system.
  - Compare with plane waves that are as non-localized as possible.
  - Orbitals can be obtained from quantum mechanical atomic calculations. (Or pseudo-atomic; see below)
  - The accuracy is not so straightforward to adjust as in the plane wave method.

Pseudopotentials

- In most cases the filled inner electron shells of atoms do not have any effect on the behavior of the system.
- The idea is to remove the core electrons and the strong nuclear potential and replace them with a weaker pseudopotential.
- Outside some cut-off radius r_c the pseudo wavefunctions and the pseudopotential are indentical to those of the real atom..

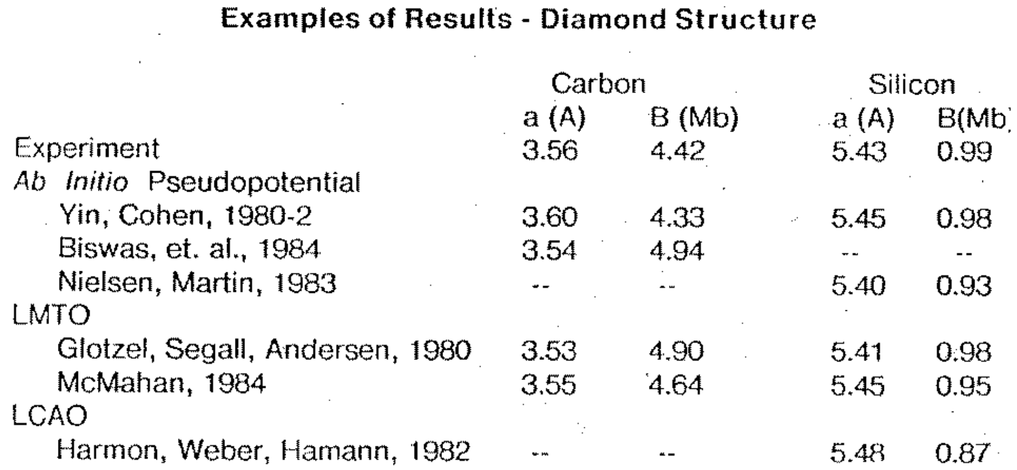
- The counterpart to pseudopotential methods are the **all electron methods.**

- Pseudopotentials are commonly used with DFT calculations both with planewaves and atomic type orbitals.



Pseudopotentials

- 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

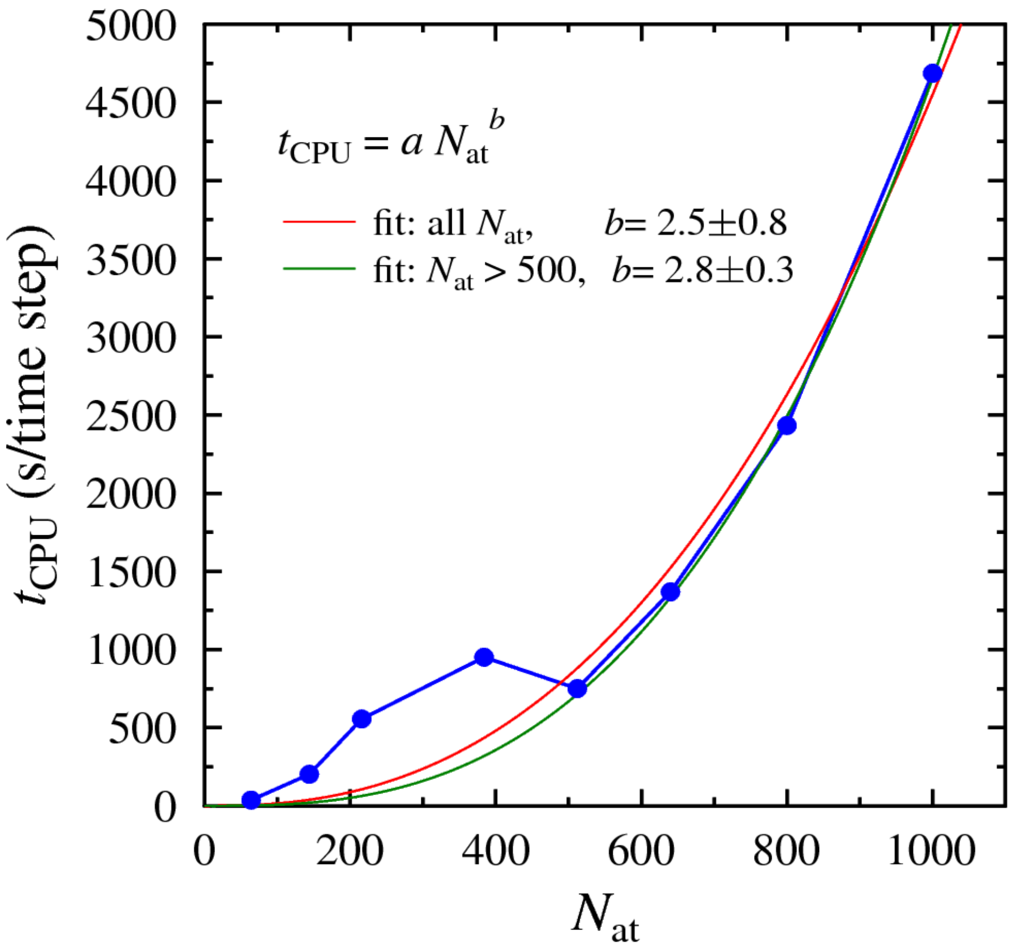
- So it is quite possible to obtain the quantities to an accuracy ~ 1 %.

- **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.

Example of scaling of a DFT calculation

- CPU time usage of a SIESTA[1] calculation:
  - Si with simple SZ basis set.
  - CPU time for one energy calculation (~ time step).
  - Simulations by E. Holmström.



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[1] **S**panish **I**nitiative for **E**lectronic **S**imulations with **T**housands of **A**toms.

Commercial HF and DFT programs

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

Commercial HF and DFT programs

- **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 Plane-wave DFT code, commercial
  - DMol^3 DFT code based on numerical basis sets, rather than Gaussian Sets
  - VASP Semi-commercial plane-wave DFT code developed in Vienna. Very widely used.
    http://cms.mpi.univie.ac.at/vasp/
  - Quantum Espresso http://www.quantum-espresso.org/
    Open Source, Free
  - GPAW Python-based code, under active development. Real-space, scales well.
    https://wiki.fysik.dtu.dk/gpaw/
  - SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms)
    - Home page: http://www.uam.es/departamentos/ciencias/fismateriac/siesta/
    - A fully self-consistent $O(N)$ DFT code. Uses LCAO basis sets.
    - Source code available, can be used as a force routine in your MD code (*parcas_siesta!*)
    - *Free for academic use.*

- **Other important stuff**
  - InsightII The graphical user interface of Accelrys Inc., from which most codes of Accelrys
    and some non-commercial codes such as DMol and Gaussian can be run.
    http://www.accelrys.com
- See also **http://electronicstructure.org/**

Tight-binding methods

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

- **Tight-binding** (**TB**) 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 eigen-values 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.

Tight-binding methods

- Bonding of H_2
  - Wave function: $|\psi\rangle = a_1|\phi_1\rangle + a_2|\phi_2\rangle$
  - Schrödinger equation

    $\hat{H}|\psi\rangle = E|\psi\rangle$
  - Project to states $|\phi_1\rangle$ and $|\phi_2\rangle$

$$\begin{cases} \langle\phi_1|\hat{H}|\psi\rangle = \langle\phi_1|E|\psi\rangle \\ \langle\phi_2|\hat{H}|\psi\rangle = \langle\phi_2|E|\psi\rangle \end{cases} \Rightarrow \begin{cases} E_0 a_1 + h a_2 = E a_1 \\ h a_1 + E_0 a_2 = E a_2 \end{cases},$$

$h = \langle\phi_1|\hat{H}|\phi_2\rangle = \langle\phi_2|\hat{H}|\phi_1\rangle$ (We know (?) that $h < 0$.)

  - Let's shift energy origin so that $E_0 = 0 \Rightarrow$ we get the equation

$$\begin{bmatrix} 0 & -|h| \\ -|h| & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$$

  - Solutions $E = \pm|h|$, $|\psi\rangle = \frac{1}{\sqrt{2}}(\phi_1 \mp \phi_2)$

Tight-binding methods

- 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.

- See for example Foulkes *et al.*, *Phys. Rev. B* **39** (1989) 12520, and Sutton *et al.*, *J. Phys. C: Solid State Phys.* **21** (1988) 35. for the DFT foundations of the TB model

Tight-binding methods

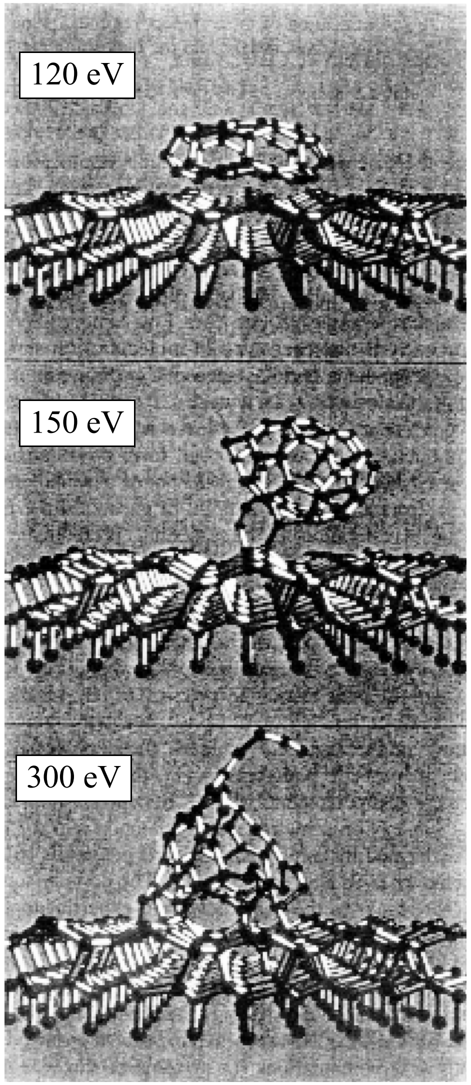
- An example of a $O(N)$ TBMD application [G. Galli and F. Mauri, *Phys. Rev. Lett.* 73 (1994) 3471]

  - A fullerene C_{60} colliding with a diamond surface with different kinetic energies $E\mathrm{k}$ (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** (**QMC**) methods are a set of DFT-related methods where Monte Carlo simulation techniques are used to minimize the correlation term of DFT.
  - 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: Diffusion Monte Carlo (DMC) and Variational Monte Carlo (VMC)
- Just an example on results [Grossman *et al.*, *Phys. Rev. Lett.* **75** (1995) 3870]:

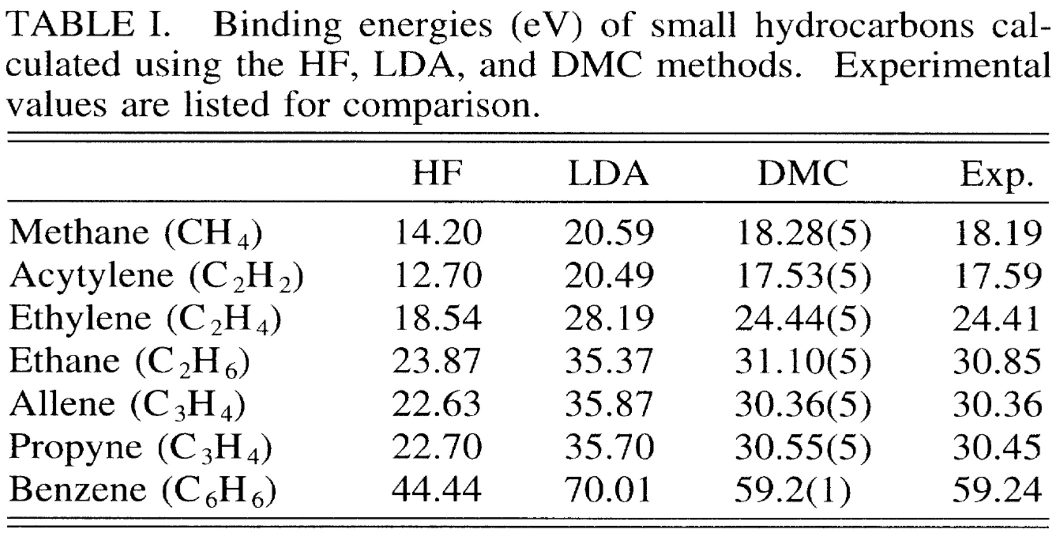


TABLE I. Binding energies (eV) of small hydrocarbons calculated using the HF, LDA, and DMC methods. Experimental values are listed for comparison.

	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

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

Very brief mention of a few other methods

- What is the minimum-energy configuration of C_{20} [Grossman *et al.*, *Phys. Rev. Lett.* 75 (1995) 3870.]?

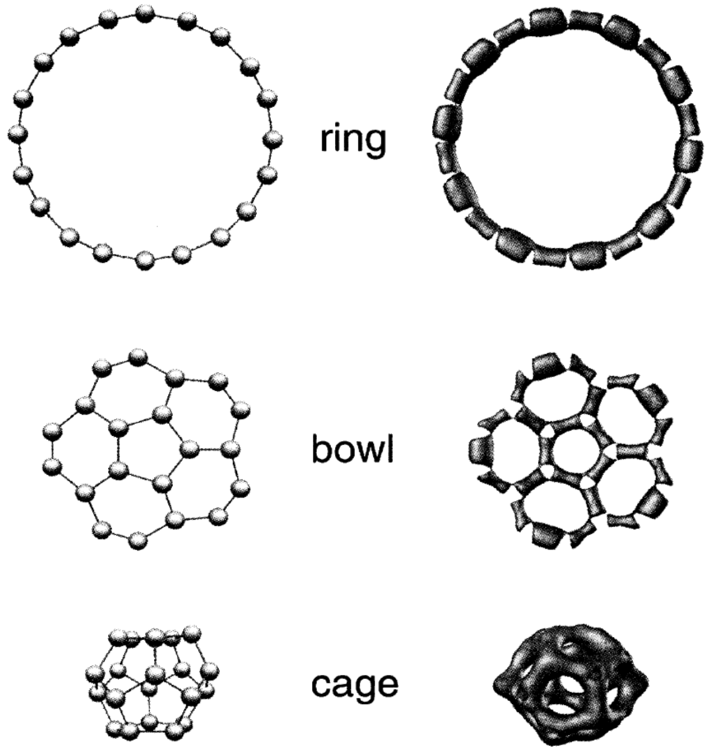


FIG. 1. The three isomers of C_{20} and their corresponding HF valence electron density isosurfaces. There are ten triple bonds in the ring and five in the bowl, and a much more covalent bonding character in the cage.

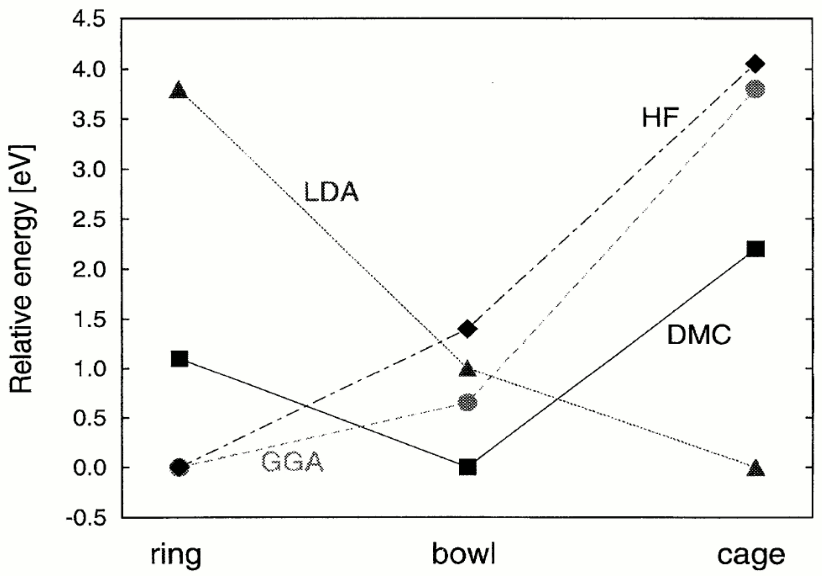


FIG. 2. The relative energy differences for the ring, bowl, and cage C_{20} isomers (DMC error bars are 0.2 eV). For each theory the lowest energy structure is taken as a reference. BLYP refers to calculations done with the Becke-Lee-Yang-Parr functional.

- 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.

Very brief mention of a few other methods

- **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