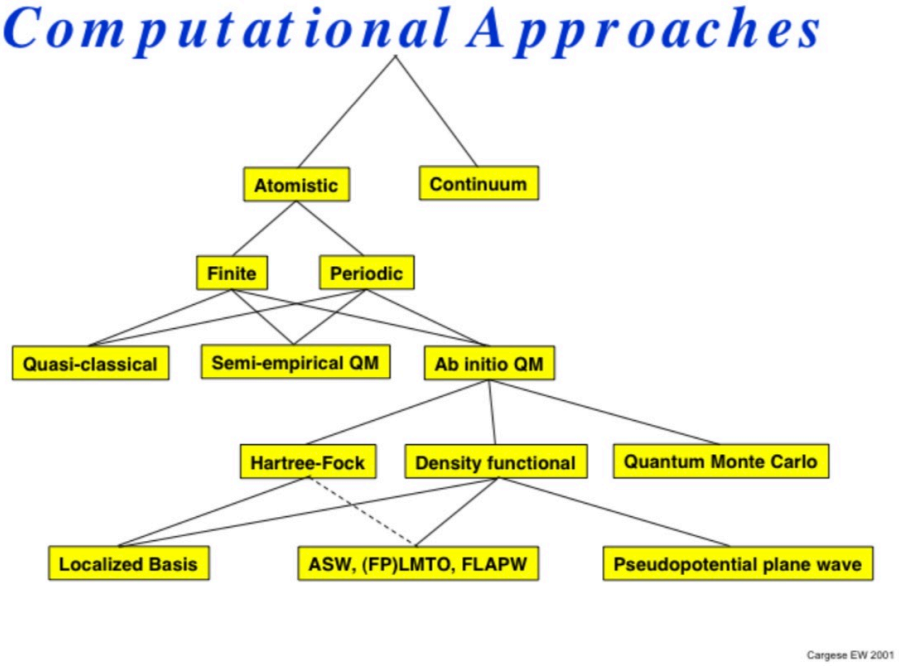
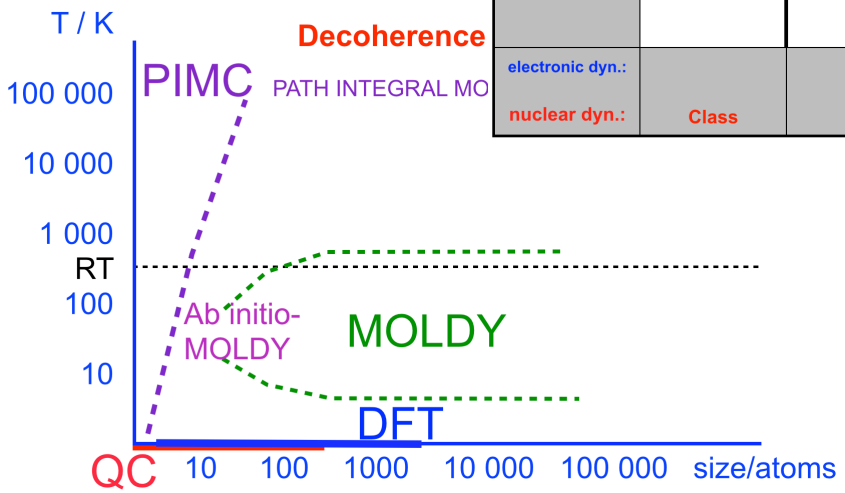
9. First-principles methods

First-principles or ab initio methods are based on most fundamental starting point, *i.e.* quantum mechanics together with constants and laws of Nature. If restricted to electronic structure of atoms and molecules, then names *ab intitio* and *quantum chemistry* are used.



Let us compare various "molecular modeling" methods by classification schemes:

time dependent	MOLECULAR	Wave packet approaches	RTPI	TDDFT	Car–Parrinello and
T > 0 equilibrium	DYNAMICS Metropolis Monte Carlo	Rovibrational approaches	PIMC		*ab initio* MOLDY
T = 0	Molecular mechanics		RTPI, DMC, VMC	*ab initio* Quantum Chemistry / DFT / semiemp.	
electronic dyn.:			Q	Q	Q
nuclear dyn.:	Class	Q	Q		Class



METHODS IN COMPUTATIONAL CHEMISTRY

- **MOLECULAR MECHANICS, DYNAMICS (& MONTE CARLO)**

  give geometries
  conformations
  dynamics

  but not electronic structure

  Newtonian mechanics

  $$M_\mu \frac{d^2\mathbf{R}_\mu}{dt^2} = -\nabla_\mu E$$

  or optimization or Metropolis Monte Carlo

- **SEMI-EMPIRICAL METHODS**

  give electronic structure
  (bonding, molec. orb.)

  but not "independent" results

  $$\begin{pmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

  with empirical α and β

- ***AB INITIO* METHODS**

  give "everything" static
  independently

  but not dynamics
  large systems
  inexpensive

  Solving

  $$\left(\sum_i^N \left(-\tfrac{1}{2} \nabla_i^2 \right) + \sum_{i,\mu}^{N,M} \left(-\frac{Z_\mu}{r_{i\mu}} \right) + \ldots \right) \Psi(\mathbf{X}) = E\,\Psi(\mathbf{X})$$

  numerically

- ***AB INITIO* MOLECULAR DYNAMICS**

  ab initio with dynamics

  $$\mu\, \ddot{\psi}_n = -\frac{\delta E}{\delta \psi_n^*} + \sum_m \Lambda_{nm}\, \psi_m$$

  $$M_\mu\, \ddot{\mathbf{R}}_\mu = -\nabla_\mu E$$

Consider solving the nonrelativistic time-independent Schrödinger equation

$$H\,\psi(\mathbf{r},\mathbf{R}) = E(\mathbf{R})\,\psi(\mathbf{r},\mathbf{R}) \tag{9.1}$$

in Born–Oppenheimer-approximation, where $\mathbf{r} = \{\mathbf{r}_i\}$ and $\mathbf{R} = \{\mathbf{R}_I\}$ are the coordinates of electrons and nuclei. Then, the electronic total energy $E(\mathbf{R})$ depends on the nuclear configuration and contributes to the *potential energy (hyper)surface* (PES).

After separation of the nuclear Coulomb repulsion, the remaining electronic hamiltonian is

$$H = -\frac{\hbar^2}{2m}\sum_i^n \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I\, e^2}{4\pi\varepsilon_0\, r_{Ii}} + \frac{1}{2}\sum_{ij}^n \frac{e^2}{4\pi\varepsilon_0\, r_{ij}}, \tag{9.2}$$

where $r_{Ii} = |\mathbf{r}_i - \mathbf{R}_I|$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\{Z_I\}$ are the nuclear charges, for a molecule with n electrons and N nuclei.

Methods of solution, where only nuclear charges, constants of nature (and fixed nuclear configuration, *i.e.* B–O approximation) are called *ab initio-* or *"first-principles"* methods. Within sc. *semiempirical methods* parts of the hamiltonian and/or wavefunction are fitted to the known experimental data.

Ab initio methods can be divided to two main formalisms: sc. *wavefunction theory*, which is based on the Hartree–Fock theory, and *density-functional theory* (DFT), where the basic concept is the electron density.

The target is finding the conformation dependent energy with the "chemical accuracy", which is 0.01 eV (~ 1 kJmol^{-1}). Then, the molecular structure and the energetics relevant for chemical reactions are found with sufficient accuracy.

Hartree–Fock SCF-method

9.1. One-electron picture

If ignoring the electron–electron repulsion, then for a nuclear configuration $\mathbf{R}$, the N electron wavefunction can be separated to one-electron wavefunctions or orbitals ψ_u^o and

$$H^o \psi^o = E^o \psi^o, \tag{9.3a}$$

where

$$H_o = \Sigma_i^N h_i \tag{9.3b}$$

and

$$h_i \psi_u^o(\mathbf{r}_i) = E_u^o \psi_u^o(\mathbf{r}_i), \tag{9.4}$$

where

$$\psi^o(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \psi_a^o(\mathbf{r}_1)\, \psi_b^o(\mathbf{r}_2) \ldots \psi_z^o(\mathbf{r}_N). \tag{9.5}$$

The one-electron wavefunction added by the spin function, is called *spin-orbital* $\phi_u(\mathbf{x}_i) = \psi_u^o(\mathbf{r}_i)\, \sigma_u(i)$. This simplified method is called *Hartree approach.*

9.2. Hartree–Fock approach

Now, the antisymmetrized N electron wavefunction ψ^o, (sec. 7.15) is written as

$$\psi^o(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N; \mathbf{R}) = (N!)^{-1/2} \det|\phi_a(\mathbf{x}_1)\, \phi_b(\mathbf{x}_2) \ldots \phi_z(\mathbf{x}_N)| = (N!)^{-1/2} \det|\phi_a(1)\, \phi_b(2) \ldots \phi_z(N)|. \tag{9.6}$$

The one-electron picture can be retained, while adding to the above hamiltonian the average Coulomb potential of orbital charge density, the *Hartree potential.* In case of atoms this is the *central-field approximation.* In Hartree–Fock method, each of the N electrons feel the Hartree potential of the other $(N–1)$ electrons. Then, we change the notation $\psi^o \to \psi$.

Now, let us find the best spin-orbitals with variation principle by minimizing the Rayleigh ratio

$$\mathcal{E} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \tag{6.43a}$$

which leads to the *Hartree–Fock equations,* (Appendix 11), *i.e.* the *one-electron equations*

$$f_i \phi_u(\mathbf{x}_i) = \varepsilon_u \phi_u(\mathbf{x}_i) \tag{9.7a}$$

for each spin-orbital ϕ_u; $u = a, b, ..., z$. Then the *Fock-operator* f_i becomes as given in sec. 7.16 and eqs. (7.47–49)

$$f_i = h_i + \Sigma_u\, [d\, J_u(i) - K_u(i)], \tag{9.7b}$$

where u runs through occupied orbitals, $d = 1$ is spin-degeneration, and *Coulomb operator* J_u and *excahange operator* K_u are

$$J_r\, \psi_s(1) = \left\{ \int \psi_r^*(2)\, \frac{e^2}{4\pi\varepsilon_0\, r_{12}}\, \psi_r(2)\, d2 \right\} \psi_s(1) \tag{9.7c}$$

and

$$K_r\, \psi_s(1) = \left\{ \int \psi_r^*(2)\, \frac{e^2}{4\pi\varepsilon_0\, r_{12}}\, \psi_s(2)\, d2 \right\} \psi_r(1). \tag{9.7d}$$

Note, that

$$J_u(i)\, \phi_u(i) = K_u(i)\, \phi_u(i).$$

The spin-orbitals should be iterated to *self-consistency* (SCF), see p. 130, sec. 7.16, and such, that in the ground state $\psi = \Phi_0$ the N lowest spin-orbitals are occupied. The occupied spin-orbitals contribute to the Fock-operator. In genenral, the Fock-operator has an infinite number of eigenstates and energies, which relate to the one-electron excited states. However, in matrix formalism the number of eigenstates and energies is restricted to the number basis functions, see sec 9.3 below.

"Restricted" and "unrestricted" Hartree–Fock

If the atomic or molecular orbitals or shells are *"closed"*, *i.e.* fully occupied, the spin state is singlet, $S = 0$, because all orbitals have the same number of α and β electrons. The Hartree–Fock wavefunction is then

$$\Phi_0 \;=\; (N!)^{-1/2}\,\det|\,\psi_a{}^{\alpha}\,\psi_a{}^{\beta}\,\psi_b{}^{\alpha}\,\psi_b{}^{\beta}\,\ldots\,\psi_z{}^{\alpha}\,\psi_z{}^{\beta}\,|.$$

In case of closed shells this is called *restricted–HF* (RHF) wavefunction, whereas the open shell *unrestricted–HF* (UHF) wavefunction is

$$\Phi_0 \;=\; (N!)^{-1/2}\,\det|\,\psi_{a1}{}^{\alpha}\,\psi_{a2}{}^{\beta}\,\psi_{b1}{}^{\alpha}\,\psi_{b2}{}^{\beta}\,\ldots\,\psi_{z1}{}^{\alpha}\,\psi_{z2}{}^{\beta}\,|.$$

The UHF one-electron orbitals may depend on spin, because of spin imbalance. Thus, *e.g.* $\psi_{a1}(\mathbf{r}) \neq \psi_{a2}(\mathbf{r})$.

The RHF wavefunction is an eigenfunction of the spin operator S^2 with an eigenvalue $S(S+1)\hbar^2$, but the UHF wavefunction is not, in general.

9.3. Roothaan equations

In lower than (atomic) spherical symmetry, *i.e.* molecules, the HF wavefunction is generally expanded in a basis set $\{\theta_j\}$. The HF equation (7.47a) for an orbital $\psi_u(\mathbf{r})$ is

$$f_k\,\psi_u(\mathbf{r}_k) \;=\; \varepsilon_u\,\psi_u(\mathbf{r}_k), \tag{9.9}$$

and thus, the form of the solution

$$\psi_u(\mathbf{r}_k) \;=\; \Sigma_j^{M}\,c_{ju}\,\theta_j(\mathbf{r}). \tag{9.8}$$

We substitute (9.8) to (9.9), multiply from the left by $\theta_i{}^*$ and integrate. We use a notation

$$S_{ij} \;=\; \int\theta_i{}^*(\mathbf{r})\,\theta_j(\mathbf{r})\,d\mathbf{r}, \tag{9.11}$$

for the overlap matrix element, and similarly for the *Fock matrix*

$$F_{ij} \;=\; \int\theta_i{}^*(\mathbf{r}_k)\,f_k\,\theta_j(\mathbf{r}_k)\,d\mathbf{r}_k. \tag{9.12}$$

Then we obtain for all $i = 1, 2, \ldots, M$; sc. *Roothaan equations*, which can be presented as a matrix equation

$$\boldsymbol{F}\,\mathbf{c}_u \;=\; \varepsilon_u\,\boldsymbol{S}\,\mathbf{c}_u, \tag{9.13a}$$

where $\boldsymbol{F} = \{F_{ij}\}$, $\boldsymbol{S} = \{S_{ij}\}$, $\mathbf{c}_u = \{c_{ju}\}$ for each $u = a, b, \ldots, z$. These M equations can also be presented in form

$$\boldsymbol{F}\,\boldsymbol{c} \;=\; \boldsymbol{S}\,\boldsymbol{c}\,\boldsymbol{\varepsilon}, \tag{9.13b}$$

where $\boldsymbol{c} = \{\mathbf{c}_u\} = \{c_{ju}\}$ and $\boldsymbol{\varepsilon} = \{\varepsilon_{ju}\}$, when $\varepsilon_{ju} = \varepsilon_u$.

The solution, eigenvalues ε_u and the corresponding eigenvectors $\mathbf{c}_u$, must be determined self-consistently (SCF), because the Fock operator, see (7.47–49), depends on the solution,

$$F_{ij} \;=\; h_{ij} + \Sigma_{\ell,m}\,P_{\ell m}\,\{\langle\, i\ell \mid 1/r_{12} \mid jm\,\rangle - \langle\, i\ell \mid 1/r_{12} \mid mj\,\rangle\} \tag{9.18}$$

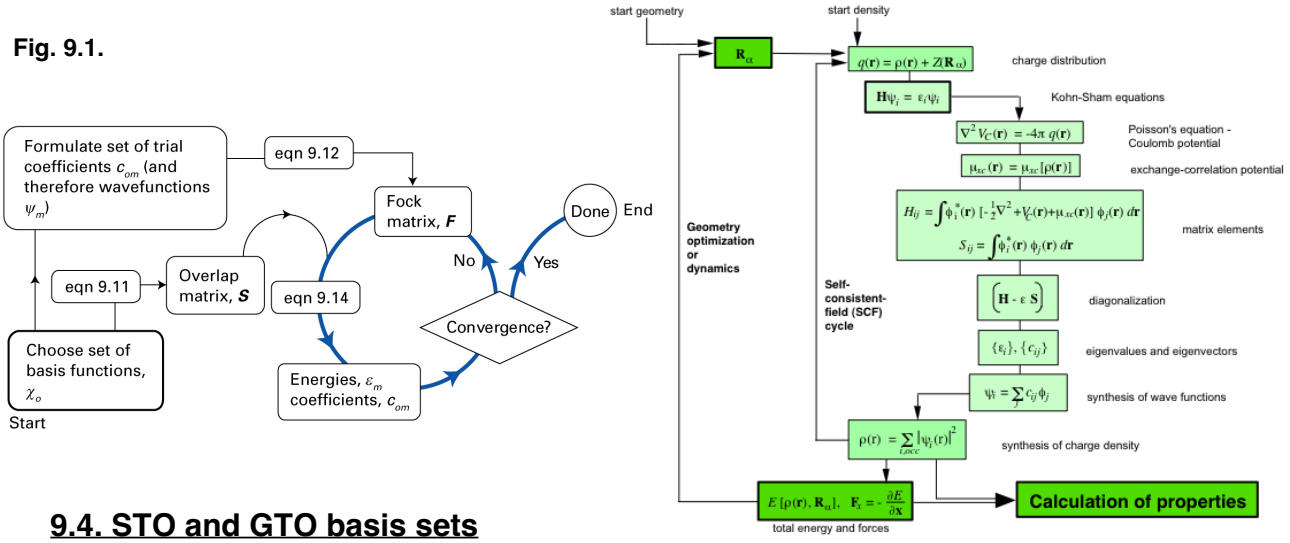
where the elements of the sc. *density matrix* are

$$P_{\ell m} \;=\; d\,\Sigma_u\,c_{\ell u}{}^*\,c_{mu}. \tag{9.19}$$

Here, d is the occupation of orbital ψ_u, usually 2.

The sc. two-electron integrals $(ij|\ell m) = \langle\, i\ell \mid 1/r_{12} \mid jm\,\rangle$ are many, of the order of M^4. Therefore, they take a significant part of the computational capacity and power.

Fig. 9.1.



9.4. STO and GTO basis sets

For an accurate, but easy presentation of molecular orbitals a good basis set is needed. In general, a complete basis consists of an infinite numer of basis functions, $M = \infty$. The solution in a complete basis set is called the *Hartree–Fock limit* and the difference from that is called as the *basis-set truncation error.*

In the basis set *Slater type orbitals* (STO) the radial part is $e^{-\zeta r}$, where ζ is *orbital exponent,* see sec 7.14. The infinite set $\{e^{-\zeta r}\}_\zeta$ is complete, if $\zeta \in \mathbb{R}$, but in practice, only a limited number of ζ_ℓ are chosen by fitting to STO.

STO is not very popular, because evaluation of two-electron integrals with STO is laborious.

Gaussian type orbitals (GTO) basis functions assume the radial part $e^{-\alpha r^2}$. Sc. *cartesian GTO functions* take the form

$$g_{ijk}(\mathbf{r}) = N\, x^i\, y^j\, z^k\, e^{-\alpha r^2}, \qquad (9.20)$$

where $\mathbf{r} = \mathbf{r}_q - \mathbf{r}_c = x\,\hat{\mathbf{i}} + y\,\hat{\mathbf{j}} + z\,\hat{\mathbf{k}}$, i, j and k are nonnegative integers, $\mathbf{r}_c$ is position of the "center", usually the nucleus, and $\mathbf{r}_q$ is position of the electron q. Now, $\ell = i + j + k$, and therefore, $\ell = 0, 1, 2, \ldots$ are s, p, d, ... type GTO functions.

If $x^i\, y^j\, z^k$ are replaced by spherical harmonics $Y_{\ell\, m_\ell}$, we have sc. *"spherical gaussians" basis set.*

The size of the Fock matrix to be diagonalized can be reduced by contraction of the basis $\{g_i\}_i$ to a smaller *"contracted GTO basis"* $\{\chi_j\}_j$ by

$$\chi_j = \Sigma_i\, d_{ji}\, g_i, \qquad (9.21)$$

where the contracted function χ_j is a sum of *primitive GTO-functions* g_i. The coefficients d_{ji} are determined by fitting χ_j to atomic orbitals.

Molecular orbitals are then written in the form

$$\psi_i = \Sigma_j\, c_{ji}\, \chi_j$$

for the coefficients c_{ji} to be searched.

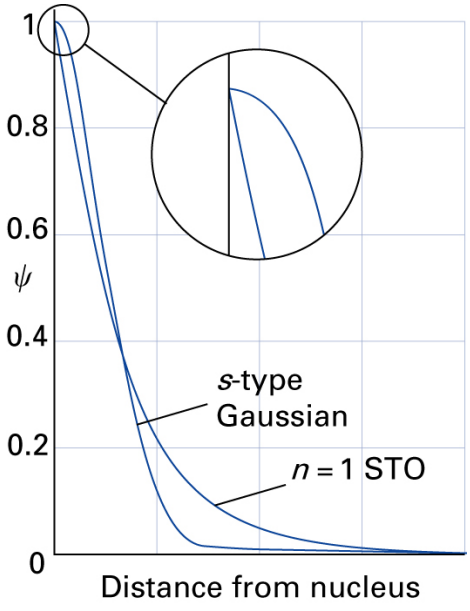


Fig. 9.4.

The basis set formation and contraction schemes of GTO are many, *e.g.:*

- minimal basis set
- DZ, double–zeta basis set
- TZ, triple–zeta basis set
- SV, split–valence basis set
- DZP, double–zeta basis set plus polarization functions
- STO–NG, *e.g.* STO–3G
- (4s)/[2s], (9s5p)/[3s2p]
- 3–21G, 6–31G*, 6–31G**

An incomplete basis set implies errors or deficiencies in the solution. One of these is sc. *"basis set superposition error",* which can be corrected by sc. *"counterpoise correction".*

Basis set	H_2	N_2	CH_4	NH_3	H_2O
STO-3G	−1.117	−107.496	−39.727	−55.454	−74.963
4-31G	−1.127	−108.754	−40.140	−56.102	−75.907
6-31G*	−1.127	−108.942	−40.195	−56.184	−76.011
6-31G**	−1.131	−108.942	−40.202	−56.195	−76.023
HF limit	−1.134	−108.997	−40.225	−56.225	−76.065

Table 9.3. HF–SCF energies (in units of Hartree = 27.21165 eV = 4.35975 aJ

Basis set	H_2	N_2	CH_4	NH_3	H_2O
STO-3G	1.346	2.143	2.047	1.952	1.871
4-31G	1.380	2.050	2.043	1.873	1.797
6-31G*	1.380	2.039	2.048	1.897	1.791
6-31G**	1.385	2.039	2.048	1.897	1.782
Observed	1.401	2.074	2.050	1.912	1.809

Table 9.4. HF–SCF bond lengths (in units of Bohr = 0.529177 Å)

Electron correlation

HF theory includes the Coulombic repulsion between electrons in an average way, in form of Hartree potential, only. This means, that the HF theory does not include the many-body effects or correlations. This is the "definition of correlations" used with the *ab initio* methods.

9.5. Configuration state functions (CSF)

Assuming the number of basis functions is n, then we have $2n$ spin-orbitals, which can be occupied with N electrons in

different ways.

Let us denote the ground state Slater determinant as Φ_o and once excited determinant as Φ_a^p and twice excited one as Φ_{ab}^{pq}, etc.

Now, the *configuration state function (CSF)* is defined as the symmetry-adapted linear combination of these determinats. These can be used as a basis set for eigenfunctions of the hamiltonian and all operators commuting with the hamiltonian, *e.g.* the operator S^2.

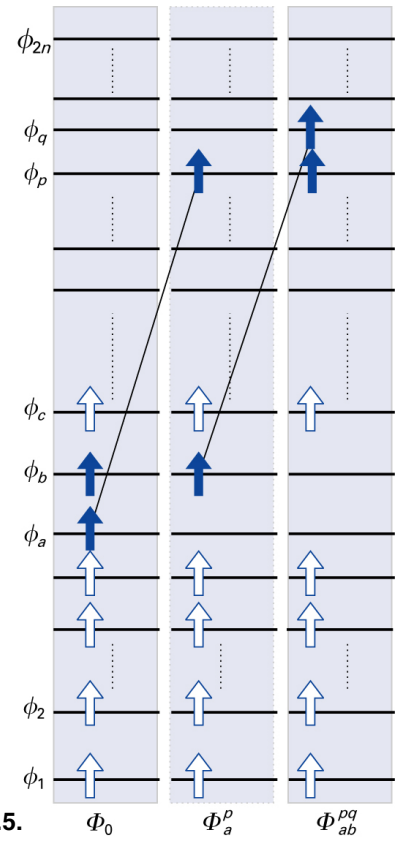


Fig. 9.5.

9.6. Configuration interaction (CI)

The exact N electron many-body wavefunction can be written as

$$\Psi = C_0\Phi_0 + \Sigma_{a,p} C_a^p \Phi_a^p + \Sigma_{a<b,p<q} C_{ab}^{pq} \Phi_{ab}^{pq} + \Sigma_{a<b<c,p<q<r} C_{abc}^{pqr} \Phi_{abc}^{pqr} + \ldots , \qquad (9.23)$$

i.e., as a linear combination of the CSFs defined above, and assuming that the one-electron basis set is complete. This means, that the CSFs or N-electron determinants form a complete *CSF-basis* for N-electron wavefunctions.

The excat many-body wavefunction Ψ does not include the one-electron picture of Hartree–Fock theory, *i.e.,* occupation configuration of one-electron orbitals, but instead, a superposition of those. Therefore, this is called *configuration mixing* or *configuration interaction* (CI).

The concepts *"full CI"* and *"basis set correlation energy"* are definend in Fig. 9.6.

Correlation phenomena can also be called structural/static, dynamic or partly both depending on the interpretation of the case.

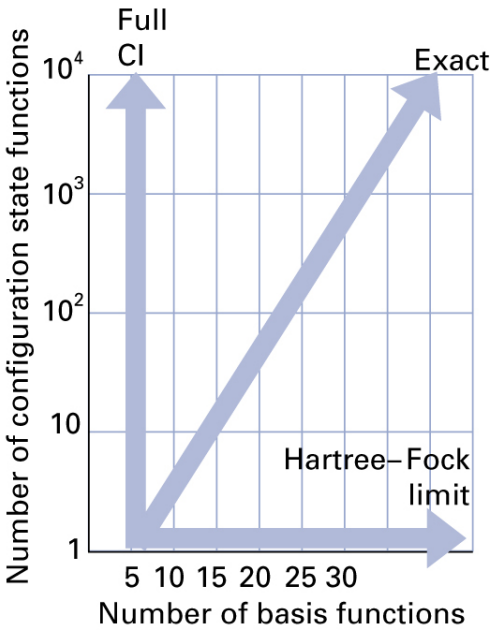


Fig. 9.6.

9.7. CI calculations

The coefficients C in CSF expansion of Ψ (9.23) are found with a similar hamiltonian matrix diagonalisation as for finding coefficients c in the expansion of spin-orbitals ψ_i in (9.8) in sec. 9.3. Many of the matrix elements vanish and the most contributing CSF "basis functions" are Φ_0 and doubly excited Φ_{ab}^{pq}. According to the Brillouin theorem $\langle \Phi_0 \mid H \mid \Phi_a^p \rangle = 0$.

Depending on truncation of series (9.23) various limited CI are called:

- DCI
- SDCI
- SDTQCI

Limited CI lack of sc. *"size-consistency".*

9.8. MCSCF and MRCI

In basic CI approach all different CSF determinants are formed from the same HF optimised spin-orbitals for Φ_0. But in case the set $\{c_{ji}\}$ in (9.8) $\psi = \Sigma_{jM} c_{ji} \theta_j$ is optimised simultaneously with $\{C_{ab\ldots}^{pq\cdots}\}$ in (9.23), the approach is called *"multiconfiguration–SCF"* (MCSCF). Thus, in MCSCF there is no ground state configuration Φ_0, which is improved with excited states.

The *"Complete active-space–SCF"* (CASSCF) is a MCSCF approach, where the spin-orbitals are grouped to *inactive, active* and *virtual,* based on how they are excited or occupied in CSF states.

Sc. *Multireference–CI"* (MRCI) is an intermediate between CI and MCSCF, which gives relatively good description of correlations with a small set of CSF functions. Thus, *e.g.* the "size-consistency" error of MRCI can be made small.

CI approaches are variational, but suffer from lack of size-consistency.

9.9. Møller–Plesset many-body perturbation theory

Many-body perturbation theory (MBPT, monihiukkashäiriöteoria) is an alternative to improve HF approach with a systematic manner. MBPT is not variational, but it is size–consistent.

In Møller–Plesset perturbation theory the reference state is chosen to be the sum of one-electron Fock operators

$$H^{(0)} = \Sigma_i f_i. \tag{9.27}$$

HF wavefunction Φ_0 is an eigenfunction of this operator, see the example 9.4 in text book. Next we choose the first order perturbation operator to be

$$H^{(1)} = H - H^{(0)}, \tag{9.28}$$

which "corrects" the reference state $H^{(0)}$ energy to the Hartree–Fock energy, where H is the molecular hamiltonian (9.2).

Thus, the Hartree–Fock energy is $E_{HF} = E^{(0)} + E^{(1)}$, where

$$E^{(0)} = \langle \Phi_0 \mid H^{(0)} \mid \Phi_0 \rangle$$

and

$$E^{(1)} = \langle \Phi_0 \mid H^{(1)} \mid \Phi_0 \rangle.$$

The second order correction is

$$E^{(2)} = \sum_{J \neq 0} \frac{\langle \psi_J | H^{(1)} | \psi_0 \rangle \langle \psi_0 | H^{(1)} | \psi_J \rangle}{E^{(0)} - E_J}, \tag{9.29}$$

where Φ_J are "excited" CSF functions. In the numerator all the matrix elements vanish except for those, where Φ_J is a doubly excited CSF. This second order MP perturbation theory is called MP2. The third and fourth order theories are correspondingly MP3 and MP4.

9.10. Coupled-Cluster method

The correlated N-electron wavefunction can also be written as

$$\Psi = e^C \Psi_0, \tag{9.30a}$$

where Ψ_0 is the Hartree-Fock wavefunction

$$e^C = 1 + C + C^2/2! + C^3/3! + \ldots, \tag{9.30b}$$

where C is "cluster operator"

$$C = C_1 + C_2 + C_3 + \ldots + C_N \tag{9.31a}$$

and C_k is k-fold excitation operator. For example,

$$C_1 \Psi_0 = \Sigma_{a,p} t_a^p \Phi_a^p \quad \text{and} \quad C_2 \Psi_0 = \Sigma_{a,b,p,q} t_{ab}^{pq} \Phi_{ab}^{pq}. \tag{9.31b}$$

It can be shown, that *e.g.* out of 2-electron excitations $C_1 C_1 \Psi_0$ and $C_2 \Psi_0$ only the latter one should be counted, the coupled one, see the diagrams in Fig. 9.8. The same rule should be followed in case of all other excitations, too.

Thus, in "coupled cluster doubles" (CCD) approximation $C = C_2$ and $\Psi \approx e^{C_2} \Psi_0$ and Schrödinger equation is written as

$$H e^C \Psi_0 = E e^C \Psi_0. \tag{9.32}$$

Due to the orthogonality conditions, that results in energy

$$E = E^{HF} + \langle \Psi_0 \mid H C_2 \mid \Psi_0 \rangle. \tag{9.33}$$

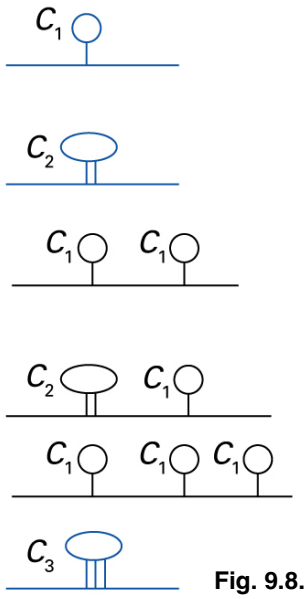


Fig. 9.8.

Density functional theory (DFT)

Density functional theory (DFT) is an alternative approach to solve the many-electron system Schrödinger equation (9.1). DFT is a natural approach for extended systems (solids, sizeable clusters or molecules), whereas the Hartree–Fock wavefunction theory and its derivatives are that for smaller systems: atoms and smaller molecules.

9.11. Hohenberg–Kohn existence theorem

The starting point is the electron density, see sec. 7.18, p. 134. All properties of the ground state system of electrons in a given external potential (*e.g.*, that of the nuclei) uniquely depend on the electron density $\rho(\mathbf{r})$. This is the first Hohenberg–Kohn theorem.

Let us prove, that the ground state electron density uniquely gives its external potential, *i.e.,* its hamiltonian, which proves the theorem. Thus, let us assume two different hamiltonians H and H' with two different ground state wavefunctions Ψ and Ψ', which lead to the same ground state density.

Then, $E_0 < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle = E_0' + \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r},$

but $E_0' < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle + \langle \Psi | H' - H | \Psi \rangle = E_0 - \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r}.$

Now, sum of these inequalities implies

$$E_0 + E_0' < E_0' + E_0,$$

which proves that the assumption of two different external potentials for a given electron density must be wrong.

9.12. Hohenberg–Kohn variational theorem

The first Hohenberg–Kohn theorem implies, that with variation of the electron density the total energy can be minimized to that of the ground state, but not below. Thus, minimizing

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r}) \, v(\mathbf{r}) \, d\mathbf{r} = E_{HK}[\rho] + \int \rho(\mathbf{r}) \, v(\mathbf{r}) \, d\mathbf{r} \qquad (9.36)$$

with the condition $\delta \{ E[\rho] - \mu \int \rho(\mathbf{r}) \, d\mathbf{r} \} = 0$ we get

$$\mu = v(\mathbf{r}) + \delta E_{HK}[\rho]/\delta\rho(\mathbf{r}), \qquad (9.37)$$

where μ is the chemical potential. *Cf.*, Thomas–Fermi theory in sec. 7.18, p. 134.

9.13. Kohn–Sham equations

Introducing one-electron orbitals of non-interacting electrons or sc. *Kohn–Sham orbitals* ψ_i the ground state total energy can be written as

$$E[\rho] = -\frac{\hbar^2}{2m} \sum_i^n \int \psi_i^*(\mathbf{r}) \, \nabla_i^2 \, \psi_i^*(\mathbf{r}) \, d\mathbf{r} - \sum_I^N \int \frac{Z_I \, e^2}{4\pi\varepsilon_0 \, r_I} \rho(\mathbf{r}) \, d\mathbf{r}$$
$$+ \frac{1}{2} \int \int \frac{e^2 \, \rho(\mathbf{r}_i) \, \rho(\mathbf{r}_j)}{4\pi\varepsilon_0 \, r_{ij}} \, d\mathbf{r}_i \, d\mathbf{r}_j + E_{xc}[\rho] \, ,$$

where $\rho(\mathbf{r}) = \Sigma_i \, |\psi_i(\mathbf{r})|^2$. The first term is the kinetic energy, the second is the potential energy, the third is *Hartree energy* and the last one is sc. *exchange and correlation energy.* Thus, the energy is a functional of electron density, $E[\rho]$.

The last term corrects the independent electrons energy to the interacting electrons energy.

Application of variational principle to the total energy, silimarly to HF earlier, here leads to the Kohn–Sham equations

$$f\,\psi_i = \varepsilon_i\,\psi_i, \tag{9.39}$$

where

$$f = -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_I^N \frac{Z_I\,e^2}{4\pi\varepsilon_0\,r_I} + \frac{1}{2}\int \frac{e^2\,\rho(\mathbf{r}_j)}{4\pi\varepsilon_0\,r_{ij}}\,d\mathbf{r}_j + V_{xc}[\rho] \tag{9.42}$$

and

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta\rho}\,. \tag{9.41}$$

If $E_{xc}[\rho]$ was known, the *exchange and correlation potential* $V_{xc}[\rho]$ could be found as its functional derivative.

Thus, with DFT we can keep the one-electron picture, although we have all the correlations fully included. Therefore, interpretation of the Kohn–Sham orbitals as *quasi-electron states* is different from the wavefunction theory. It can be shown, *e.g.,* that the eigenenergy of the highest occupied Kohn–Sham orbital is the first ionization energy, exactly!

Historically, the DFT was preceded by the Thomas–Fermi method, see sec. 7.18, where however, calculation of the kinetic energy without the one-electron picture is not simple.

The sc. X_α-method derived from the HF theory by Slater is also reminiscent of DFT or LDA, see the next sec. X_α-method includes exchange energy as a functional of electron density. Also, hungarian Gáspár had presented similar suggestion even before Slater.

9.14. Local-density approximation (LDA)

For DFT calculations the exchange and correlation energy functional $E_{xc}[\rho]$ needs to be known for a given $\rho(\mathbf{r})$. This functional is known very accurately for the homogeneous electron gas (HEG), which can be described with a single parameter ρ_0 or $r_s = (3 / 4\pi\rho_0)^{1/3}$. In fact, the energies per electron in HEG $\varepsilon_{xc}[\rho_0] = \varepsilon_x[\rho_0] + \varepsilon_c[\rho_0]$ are known and the functional is then

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\,\varepsilon_{xc}^{LDA}(\rho(\mathbf{r}))\,d\mathbf{r}, \tag{9.43a}$$

where $\varepsilon_{xc}^{LDA}(\rho(\mathbf{r})) = \varepsilon_{xc}[\rho_0]$, when $\rho_0 = \rho(\mathbf{r})$. Thus, at every position $\mathbf{r}$ the ε_{xc} is approximated by that of the HEG, when $\rho_0 = \rho(\mathbf{r})$. This is the LDA.

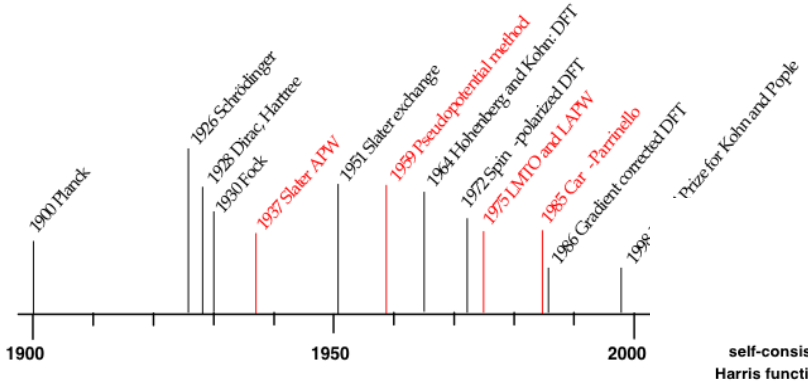
The LDA can be expected to be viable for conduction electrons of metals, for example, but it has turned out to be very useful in many other cases as well and for molecules, in particular. In general, LDA can be expected to be viable, in cases where the exchange and correlation hole is localized around the electron.

While HF approach is accurate for an one-electron system, *e.g.* hydrogen atom, the LDA is exact for an infinite HEG. Between these extremes the structure dependent correlations need to be considered and HF is completed with CI, for example. So far, the corrections to LDA are based on the "nonlocal" functionals of the form $\varepsilon_{xc}^{NL}[\rho(\mathbf{r}); \nabla\rho(\mathbf{r})]$ and many kind of hybrids of HF and DFT. The DMFT approaches are under fast development, nowadays.

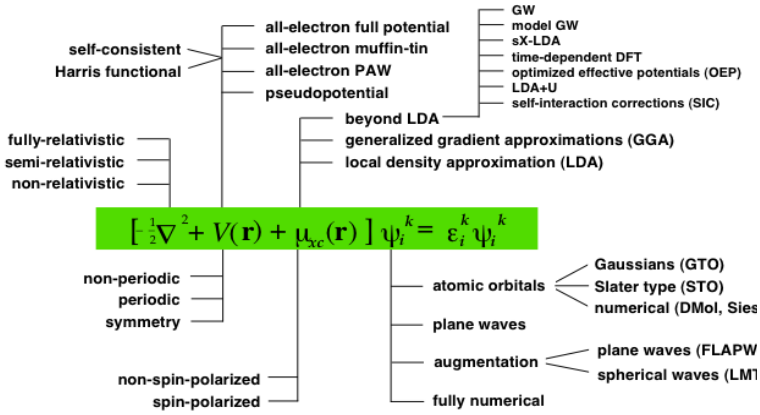
Jokingly, we can say that the hamiltonian of wavefunction theories is exact, but the resulting wavefunctions are not, whereas in case of DFT it is *vice versa,* the hamiltonian is approximate (due to the functional $V_{xc}[\rho]$), but the resulting wavefunction is exact (for that hamiltonian, within numerical accuracy).

Evolution of Quantum Theory

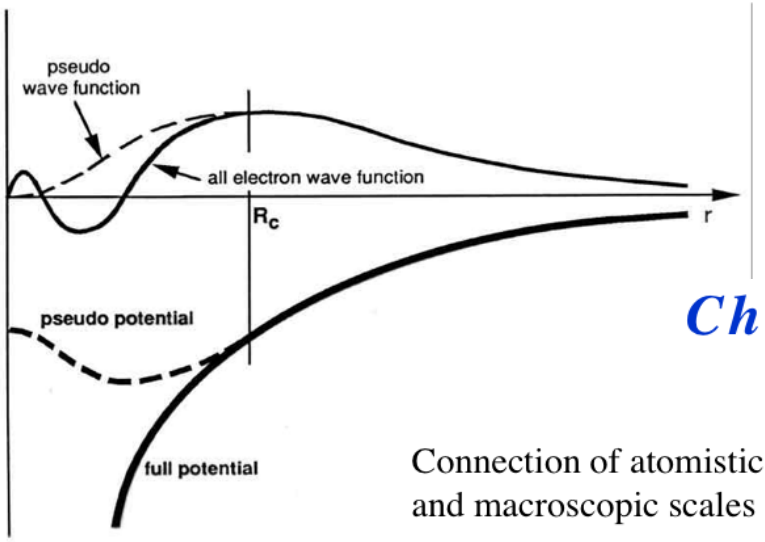
M. Planck Louis de Broglie E. Schrödinger P. A. M. Dirac D. Hartree W. Kohn J. Pople



DFT Implementations

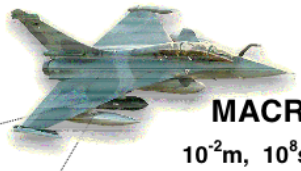


Pseudopotentials

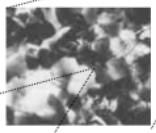


Challenge

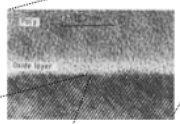
Connection of atomistic and macroscopic scales



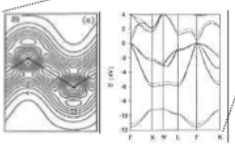
MACRO
10^{-2}m, 10^{8}s



MESO
10^{-6}m, 10^{0}s



ATOMS
10^{-9}m, 10^{-12}s



ELECTRONS
10^{-10}m, 10^{-15}s