

2 Fundamentals of Quantum Chemistry

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1 Introduction

When the Schrödinger equation and quantum mechanics were invented, the hydrogen atom was the first system targeted. The field of quantum chemistry may be considered to start also at this point, or alternatively when the first molecule, H_2 , was addressed.

The research in this field involves enormous calculations, and thus a major advance came with electronic computers. Programming languages and compilers facilitate code development, and since a few decades, computer codes for electronic structure calculations have been developed and continuously grow.

This chapter will deal with quantum chemical methods. They usually start from a Hartree-Fock calculation, and are followed by a correlation (post-Hartree-Fock) calculation. This way of including electron correlation is wave function based. As a numerical tool, basis sets (usually Gaussian basis sets) are introduced. The notion *ab initio* calculations is used in this context, with the denotation that there are no parameters fitted to experiment.

Density functional theory is at the border of quantum chemistry, and will be treated in other chapters of this book. A short section on density functional theory has been included also in this chapter, to establish the connection between Hartree-Fock and density functional theory.

This chapter aims at introducing basic notions of the field. For further reading, a couple of textbooks can be recommended, e.g. [1–6].

2 Setting up the Hamiltonian

For the electronic structure problem, we will consider a total energy expression which initially consists of kinetic energy contributions (electrons, nuclei) and the Coulomb interaction.

In a simple example, we consider two atoms (figure 1).

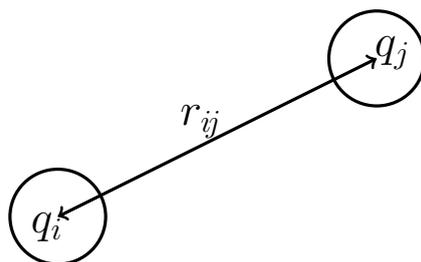


Fig. 1: A simple example with two atoms, separated by a distance r_{ij} .

The Coulomb interaction of the nuclei can be expressed as

$$V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} =: \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where atomic units ($\hbar = m_{el} = e = 4\pi\epsilon_0 = 1$) have been used in the last step.

The kinetic energy consists of contributions due to the nuclei and N electrons

$$E_{\text{kinetic}} = \frac{1}{2} M_i \vec{v}_i^2 + \frac{1}{2} M_j \vec{v}_j^2 + \sum_{k=1}^N \frac{1}{2} m_{el} \vec{v}_k^2. \quad (2)$$

In general, we obtain

$$E = E_{\text{kinetic}} + E_{\text{Coulomb}} \left(+E_{\text{external fields}} + E_{\text{relativistic corrections}} \right). \quad (3)$$

In the following, external fields (e.g. electric or magnetic fields) will not be considered, also relativistic effects are neglected. The classical energy then becomes, for a system of n nuclei of charges Z_j , and N electrons

$$E = \frac{1}{2} \sum_{j=1}^n \frac{\vec{p}_j^2}{M_j} + \frac{1}{2} \sum_{i=1}^N \frac{\vec{p}_{el,i}^2}{m_{el}} + \sum_{j=1}^n \sum_{j'=j+1}^n \frac{Z_j Z_{j'}}{|\vec{R}_j - \vec{R}_{j'}|} + \sum_{i=1}^N \sum_{i'=i+1}^N \frac{1}{|\vec{r}_i - \vec{r}_{i'}|} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_j}{|\vec{r}_i - \vec{R}_j|} \quad (4)$$

As the masses of the nuclei M_j are much larger than the masses of the electrons m_{el} , the kinetic energy of the nuclei is neglected: the Born-Oppenheimer approximation is made.

After replacing the momentum \vec{p} with the corresponding quantum mechanical operator $-i\hbar\nabla$, we obtain the quantum mechanical Hamiltonian, in atomic units,

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{\substack{j,j'=1 \\ j'>j}}^n \frac{Z_j Z_{j'}}{|\vec{R}_j - \vec{R}_{j'}|} + \sum_{\substack{i,i'=1 \\ i'>i}}^N \frac{1}{|\vec{r}_i - \vec{r}_{i'}|} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_j}{|\vec{r}_i - \vec{R}_j|}. \quad (5)$$

Finally, the Schrödinger equation is obtained

$$H\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = E\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \quad (6)$$

with the many-body wave function $\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ where \vec{x} represents the spatial coordinate \vec{r} and the spin s .

An analytical solution is possible only in few exceptional cases, such as the hydrogen atom. Remember that even the classical 3-body problem can, in general, not be solved exactly. Consequently, from the time quantum mechanics was introduced, also methods to tackle the many-body problem have been developed.

3 Quantum chemical approach

The target is the description of real materials, without employing parameters from the experiment. Quantum chemistry started with the description of atoms and molecules, and meanwhile has been extended to systems with periodicity such as 3D (bulk), 2D (surfaces), or 1D (e.g. nanotubes).

Originally, the notion quantum chemistry was restricted to wave function based methods. The first step is the description of a system with a single Slater determinant, the Hartree-Fock approach. In the next step, based on the Hartree-Fock wave function, more than one Slater determinant is considered, by post-Hartree-Fock methods (correlation methods). There has been an enormous development in this area, and is still ongoing, to perform high-level calculations for demanding systems. The strength is that these calculations are mathematically well defined, and can be systematically improved.

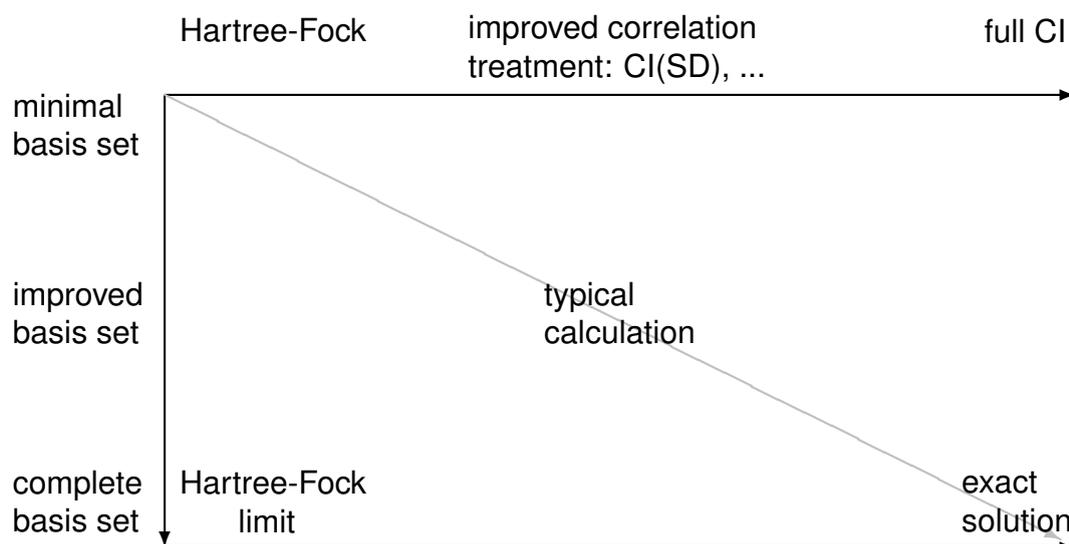


Fig. 2: Hierarchies of methods and computational parameters (basis set).

Closely related is density functional theory, which has become the main tool for electronic structure calculations. It is based on the Hohenberg-Kohn theorem [7] that an (unknown) functional should describe a system in its ground state. In this book chapter, this method will however be only marginally described, as there are other contributions in the present autumn school, or also in last year's edition [8]. Nevertheless, there are close connections also concerning implementation issues (Hartree-Fock versus density functional theory in the Kohn-Sham formulation), so that density functional theory will be addressed in this chapter.

Finally, there are further methods which will not be discussed here, such as quantum Monte Carlo. Also, semiempirical methods, methods based on force fields, or combinations of quantum mechanical methods with molecular mechanics (QM/MM) will not be included.

A hierarchy of methods can be constructed with increasing accuracy, but usually also increasing computational demand. Besides the approximation due to the method employed, it is also usually necessary to make an approximation concerning the computational parameters. In quantum chemistry, the main parameter set are the basis functions which are used to express the wave function and the orbitals. This leads to a second hierarchy concerning the choice of the basis set. The situation is visualized in figure 2: The basic method is Hartree-Fock, followed by methods such as configuration interaction (CI) with singles and doubles substitution, CI(SD), up to full configuration interaction as the maximum for a given basis set. On the basis set side, the smallest possible basis set has one basis function per orbital (minimal basis set), up to high-level basis sets which have multiple basis functions at least for the valence orbitals, and also span a large range of angular momenta.

Besides, there are further parameters such as the way integrals are computed, approximated, or possibly even discarded if they are below a certain threshold. If a numerical integration is done, then the grid size plays an important role. In calculations for periodic systems, there are further parameters such as the number of points in the reciprocal lattice.

4 Hartree-Fock

In the following, we assume, for simplicity, that the Hamiltonian is spin-independent. A single electron is described by a spin orbital $\chi(\vec{x}) = \psi(\vec{r})\alpha(s)$, with a spatial part ψ and a spin part α . The spatial orbitals are assumed to be orthonormal, as well as the spin parts. The integration is performed over $d\vec{x}$ which consists of an integral over space d^3r and over spin. The latter gives 1 if both spins are the same (both up, both down), and 0 if the spins are different (one up, the other down). The wave function is then expressed as a Slater determinant

$$\Psi_{HF}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (7)$$

This is evaluated as a determinant with the corresponding rules for the sign. Note that electrons are fermions, and thus the wave function is supposed to change sign when two electrons are exchanged. This way, the Pauli principle is included: if there were two electrons in the same spin orbital (e.g. $\chi_1 = \chi_2$), then there would be two identical columns and the wave function would be identical to zero.

The total energy, on the Hartree-Fock level, is then obtained as the expectation value of the Hamiltonian

$$E_{total, HF} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle. \quad (8)$$

As Ψ_{HF} is normalized, this expectation value is an upper bound of the total energy, as guaranteed by the variational principle.

4.1 Hartree-Fock equations

The Hartree-Fock energy has to be minimized by varying the spin orbitals χ_i , under the condition that they must remain orthonormal

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}. \quad (9)$$

This is important to guarantee the normalization of the Slater determinant. We may take this condition into account with the help of Lagrange multipliers, ε_{ba} , so that we obtain

$$L = E_{total, HF} - \sum_{a,b=1}^N \varepsilon_{ba} \left(\langle \chi_a | \chi_b \rangle - \delta_{ab} \right). \quad (10)$$

We will in the following assume the simplest case of closed-shell restricted Hartree-Fock. Restricted means that spatial orbitals for up- and down-spin are the same, reflecting the symmetry of the spin-independent Hamiltonian. Closed-shell means that each spatial orbital is either occupied with two electrons of opposing spin, or is empty.

The Hartree-Fock energy is obtained in terms of the spin orbitals as [1]

$$\begin{aligned}
E_{total, HF} = E_{NN} &+ \sum_{a=1}^N \int \chi_a^*(\vec{x}) (H_{kin} + H_{el-nuc}) \chi_a(\vec{x}) d\vec{x} \\
&+ \frac{1}{2} \sum_{a,b=1}^N \iint \frac{\chi_a^*(\vec{x}_1) \chi_a(\vec{x}_1) \chi_b^*(\vec{x}_2) \chi_b(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_1 d\vec{x}_2 \\
&- \frac{1}{2} \sum_{a,b=1}^N \iint \frac{\chi_a^*(\vec{x}_1) \chi_b(\vec{x}_1) \chi_b^*(\vec{x}_2) \chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_1 d\vec{x}_2. \tag{11}
\end{aligned}$$

Besides the nuclear-nuclear repulsion, kinetic energy and electron-nuclear attraction, we have the Coulomb repulsion between the electrons. The last term is due to the antisymmetry of the wave function, and is called the exchange term. The Coulomb term is similar to the Coulomb interaction in classical electrodynamics. There is however no classical analogue for the exchange term, and it is thus a quantum mechanical effect.

Equation (11) is the energy expression for a single Slater determinant. A better, but also more demanding approach would be to include more than one Slater determinant, see section 7. They include effects beyond Hartree-Fock, i.e. correlation effects. These correlations reflect the fact that the electrons are not independent, but instead the probability to find an electron at a certain position depends on the positions of the other electrons.

The variation δL of (10) is obtained by varying the spin orbitals

$$\chi \rightarrow \chi + \delta\chi. \tag{12}$$

This results for $\delta E_{total, HF}$ in

$$(H_{kin} + H_{el-nuc}) \chi_a(\vec{x}_1) + \sum_{b \neq a}^N \int \frac{\chi_b^*(\vec{x}_2) \chi_b(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_a(\vec{x}_1) - \sum_{b \neq a}^N \int \frac{\chi_b^*(\vec{x}_2) \chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_b(\vec{x}_1). \tag{13}$$

With the local (i.e. defined at a point \vec{r}_1) Coulomb potential

$$J_b(\vec{x}_1) = \int \frac{\chi_b^*(\vec{x}_2) \chi_b(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \tag{14}$$

and the non-local exchange potential (non-local meaning that it cannot be written as a potential at some local point \vec{r}_1)

$$K_b(\vec{x}_1) \chi_a(\vec{x}_1) = \int \frac{\chi_b^*(\vec{x}_2) \chi_a(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{x}_2 \chi_b(\vec{x}_1) \tag{15}$$

we finally obtain the Hartree-Fock equations

$$(H_{kin} + H_{el-nuc}) \chi_a(x_1) + \sum_{b \neq a}^N J_b(\vec{x}_1) \chi_a(\vec{x}_1) - \sum_{b \neq a}^N K_b(\vec{x}_1) \chi_a(\vec{x}_1) = \varepsilon_a \chi_a(\vec{x}_1). \tag{16}$$

Note that ε_{ab} does not appear, but only ε_a . This is due to a unitary transformation of the orbitals in such a way that ε_{ab} becomes diagonal and is replaced by ε_a . These orbitals are called canonical orbitals. They may be transformed to other orbital sets with the same Hartree-Fock energy. In fact, any unitary transformation among the occupied orbitals leaves the Slater determinant unchanged. Such a different choice may be more convenient, for example localized orbitals for correlation calculations.

A shorthand notation of the Hartree-Fock equations is

$$f(\vec{x}_1)\chi_a(\vec{x}_1) = \varepsilon_a(\vec{x}_1)\chi_a(\vec{x}_1). \quad (17)$$

Here we have introduced the Fock operator f . It acts on a spin orbital, but also depends on the other spin orbitals. This equation is thus not simply an eigenvalue equation, but an integro-differential equation. The Hartree-Fock equations can normally only be solved numerically.

4.2 Finite basis set: Hartree-Fock-Roothaan

The Hartree-Fock equations are usually solved by employing a finite basis set. The spatial orbitals are expressed with the help of a set of K basis functions $\phi_\nu(\vec{r})$

$$\psi_i(\vec{r}) = \sum_{\nu=1}^K c_{\nu i} \phi_\nu(\vec{r}). \quad (18)$$

After integrating with $\int d^3r \phi_\mu^*(\vec{r})$, we obtain the Fock matrix

$$F_{\mu\nu} = \int \phi_\mu^*(\vec{r}) f(\vec{r}) \phi_\nu(\vec{r}) d^3r \quad (19)$$

and the overlap matrix

$$S_{\mu\nu} = \int \phi_\mu^*(\vec{r}) \phi_\nu(\vec{r}) d^3r. \quad (20)$$

The Hartree-Fock equations (17) with a finite basis set thus may be written in matrix form

$$\sum_{\nu=1}^K F_{\mu\nu} c_{\nu i} = \varepsilon_i \sum_{\nu=1}^K S_{\mu\nu} c_{\nu i} \quad (21)$$

The coefficients $c_{\nu i}$ and the eigenvalues ε_i have to be determined by solving this generalized eigenvalue problem. An analogous procedure may be performed for periodic systems. The equation then additionally depends on the reciprocal lattice vectors \vec{k}

$$\sum_{\nu=1}^K F_{\mu\nu}(\vec{k}) c_{\nu i}(\vec{k}) = \varepsilon_i(\vec{k}) \sum_{\nu=1}^K S_{\mu\nu}(\vec{k}) c_{\nu i}(\vec{k}) \quad (22)$$

and the eigenvalues $\varepsilon_i(\vec{k})$ are interpreted as the band structure.

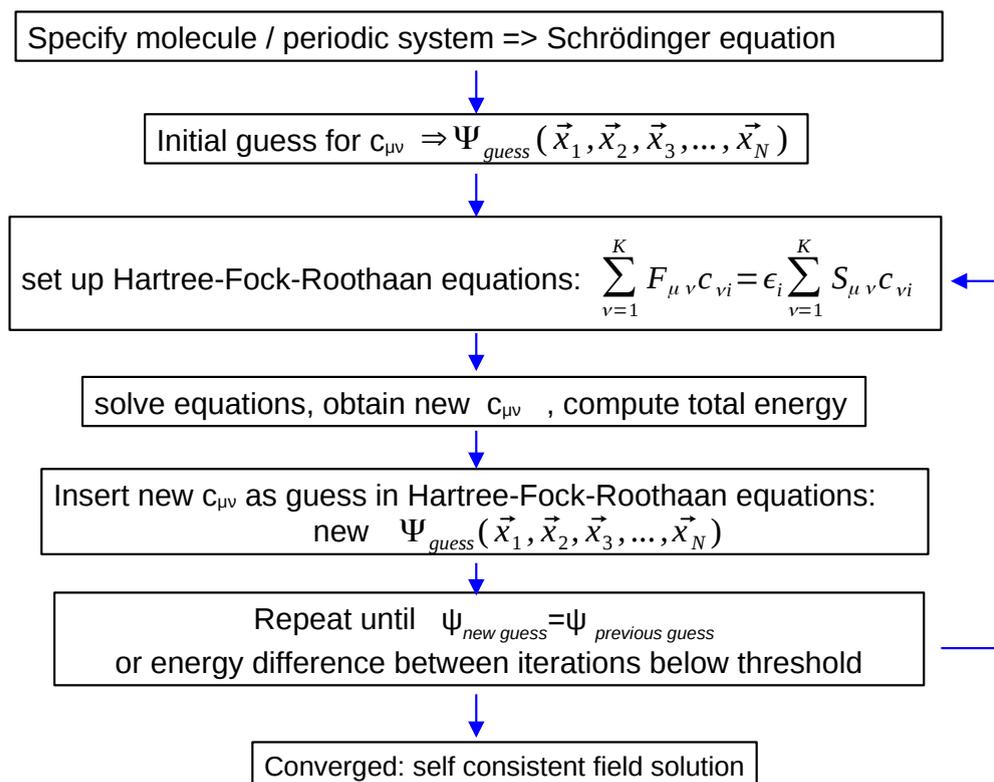


Fig. 3: *The self-consistent field procedure.*

4.3 Solution of the Hartree-Fock equations

Even after introducing a finite basis set, the Hartree-Fock equations (21) and (22) cannot be solved analytically. Instead, an iterative procedure is performed as displayed in figure 3.

After specifying the geometry and setting up the Schrödinger equation, the computational parameters are defined (basis set and other parameters). It may be advantageous to compute integrals (matrix elements of the various one and two-electron operators) beforehand and store them on disk. After this, an initial guess for the unknown coefficients $c_{\mu\nu}$ is made. The Fock matrix is constructed based on the initial guess (remember that the Fock matrix $F_{\mu\nu}$ depends on the $c_{\mu\nu}$). The Hartree-Fock-Roothaan equations are solved, and new coefficients $c_{\mu\nu}$ are obtained, together with the orbital eigenvalues ϵ_i . The new solution is used to set up the Fock operator once again, and the procedure is repeated. This is iteratively done until the energy difference between two iterations is below a threshold, or the change of the coefficients $c_{\mu\nu}$ is below a threshold (self-consistency).

The procedure works reasonably well for molecules with large gaps between highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO). Near-degeneracies, on the other hand, usually cause convergence problems. These convergence problems may be addressed by mixing the previous guess with a certain weight (Fock matrix mixing), or more sophisticated methods such as the direct inversion in the iterative subspace (DIIS) [9]. Also, level shifting is often used, e.g., in the case of transition metals. Here, the orbital eigenvalues of the unoccupied orbitals are shifted by a certain value to help finding the right occupancy; in spin-polarized systems, a different level shift is chosen for up and down spins.

5 Density functional theory

Density functional theory was initially mainly applied in solid state physics, but has meanwhile gained more and more importance in molecular electronic structure theory.

It is based on the Hohenberg-Kohn theorem [7], which shows that the energy can be written as a functional of the electron density $\rho(\vec{r})$

$$E_{total} = E[\rho] = E_{nn} + E_{kin}[\rho] + E_{ee}[\rho] + E_{ne}[\rho] \quad (23)$$

with contributions from the nuclear-nuclear repulsion E_{nn} , the kinetic energy of the electrons E_{kin} , the electron-electron repulsion E_{ee} and the attraction of the electrons by the nuclei, E_{ne} , as an external potential.

The important finding was that two external potentials which differ by more than a constant will result in different ground-state densities [7]. There is thus a one-to-one correspondence between the external potential and the electron density of the corresponding ground state. The variational principle states that the exact density minimizes E_{total} . However, the exact functional is unknown.

Kohn and Sham [10] then suggested to express the exact density as that of non-interacting electrons

$$\rho(\vec{r}) = \sum_{i=1}^N |\chi_i(\vec{r})|^2. \quad (24)$$

This corresponds to the density obtained from a reference system described by a single Slater determinant constructed from the N orbitals χ_i . We assume again, for simplicity, the case without explicit spin-dependence (i.e. closed-shell, restricted DFT), and use the notation $\chi(\vec{r})$ for the spin orbitals.

The kinetic energy is then obtained as

$$E_{kin} = -\frac{1}{2} \sum_{i=1}^N \int \chi_i(\vec{r}) \Delta \chi_i(\vec{r}) d^3r. \quad (25)$$

This is the expression for a non-interacting system, and would not be the correct one for an interacting system which, in general, has to be described by more than one Slater determinant. However, we have the correct density. As there is a one-to-one correspondence between the density and the potential, we still have the correct potential, though the kinetic energy expression alone is incorrect. The error is fixed by adding the difference between the correct kinetic energy and that of the non-interacting system into the term which describes the electron-electron interaction.

The nuclear-electron attraction is obtained simply as

$$E_{ne}[\rho] = - \sum_{j=1}^n \int \frac{Z_j \rho(\vec{r})}{|\vec{r} - \vec{R}_j|} d^3r. \quad (26)$$

while the electron-electron interaction is finally expressed as

$$E_{ee}[\rho] = E_H[\rho] + E_{XC}[\rho] \quad (27)$$

with the electron-electron Coulomb interaction (Hartree energy)

$$E_H = \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r'. \quad (28)$$

The unknown term for the exchange and correlation energy (which, as mentioned above, also includes the correction for the kinetic energy) is thus $E_{XC}[\rho]$.

As the exact density minimizes the energy, the density is obtained by a variation. Because the density is expressed with the help of the spin orbitals $\chi(\vec{r})$, the procedure is similar to Hartree-Fock theory. In the end, the Kohn-Sham equations are obtained

$$\left(-\frac{1}{2}\Delta + V_{eff}(\vec{r}) \right) \chi_i(\vec{r}) = \varepsilon_i \chi_i(\vec{r}) \quad (29)$$

with the effective potential

$$V_{eff}(\vec{r}) = -\sum_{j=1}^n \frac{Z_j}{|\vec{r}-\vec{R}_j|} + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' + \frac{\delta E_{XC}[\rho]}{\delta \rho}. \quad (30)$$

The unknown part is thus the exchange-correlation functional E_{XC} . Numerous functionals have been suggested, and the number of functionals is still growing enormously.

Note the similarity between the Kohn-Sham equations in equation (29) and the Hartree-Fock equations in equation (17). This has also practical implications: a code which solves the Hartree-Fock equations can usually be modified to perform also density functional calculations. The reverse, i.e., going from a density functional code to a Hartree-Fock code, is significantly more difficult, as the exact Fock exchange (15), which is non-local, has to be implemented.

Nowadays, most calculations are performed on the density functional level, and pure Hartree-Fock is rarely used. Due to the unknown exchange-correlation functional, an error is introduced. The order of magnitude of this error may be estimated by comparing different functionals and thus obtaining a band width of results. Particularly sensitive properties are band gaps or excitation energies which are difficult to describe in density functional theory. Functionals such as the local density approximation or gradient corrected functionals tend to underestimate gaps, whereas Hartree-Fock tends to overestimate. Though there are hybrid functionals with an admixture of Fock exchange and which often give surprisingly good values for band gaps, one still has to keep in mind that these functionals have to be calibrated and are not as systematic as wave function based correlation.

The major importance of Hartree-Fock theory is nowadays that it serves as a starting point for correlation calculations which will be discussed in Sec. 7.

6 Basis sets

As the Hartree-Fock (or Kohn-Sham) equations can, in general, not be solved analytically, the molecular (or crystalline) orbitals are instead expanded in basis functions. For a recent

overview, see [11]. In molecular quantum chemistry, local basis sets are preferably used. They can be applied to periodic systems as well – one just has to construct Bloch functions. Alternatively, plane waves are often used as basis functions in solid state applications. Here, the crystalline orbitals are expressed as

$$\Phi(\vec{r}, \vec{k}) = \sum_{\vec{K}} c_{\vec{k}, \vec{K}} \exp\left(-i(\vec{k} + \vec{K})\vec{r}\right) \quad (31)$$

where the sum over reciprocal lattice vectors \vec{K} is truncated according to the condition

$$\frac{\hbar^2}{2m_{el}}(\vec{k} + \vec{K})^2 \leq E_{\text{cutoff}} \quad (32)$$

with a cutoff energy E_{cutoff} .

In the following, the focus will be on local basis sets. An obvious starting point would be to use properties of the functions which are solutions of the hydrogen atom. Thus, basis functions of the following form have been suggested

$$\phi(\vec{r} - \vec{A}) = N(x - A_x)^a (y - A_y)^b (z - A_z)^c \exp(-\zeta|\vec{r} - \vec{A}|), \quad (33)$$

where \vec{A} is the position of the nucleus, and a , b , c are integers. Exponents are traditionally labeled with ζ . These functions are called Slater functions or Slater type orbitals. The factor $\exp(-\zeta|\vec{r} - \vec{A}|)$ has the shape of the exact solution of the hydrogen atom. Most importantly, when approaching the positions of the nuclei, Slater functions may satisfy the cusp conditions (see below) which is a major advantage. However, they suffer from the drawback that integrals are difficult to evaluate.

Gaussian basis functions

Instead, Gaussian basis functions have become very popular, as integrals are easier to be evaluated. Their structure is

$$\phi_{\text{primitive}}(\vec{r} - \vec{A}) = N(x - A_x)^a (y - A_y)^b (z - A_z)^c \exp(-\zeta(\vec{r} - \vec{A})^2) \quad (34)$$

They have various shortcomings such as that their derivative exists at the position nucleus, whereas this is in general not the case for the exact solution: Instead, a cusp condition should be fulfilled at the nucleus [2]

$$\lim_{r \rightarrow 0} \left(\frac{\partial \Psi}{\partial r} \right)_{\text{ave}} = -Z \Psi(r=0) \quad (35)$$

where ave means the spherical average, and this holds if $\Psi(r=0) \neq 0$. Similarly, the electronic cusp condition

$$\lim_{r_{12} \rightarrow 0} \left(\frac{\partial \Psi}{\partial r_{12}} \right)_{\text{ave}} = \frac{1}{2} \Psi(r_{12}=0) \quad (36)$$

with $r_{12} = |\vec{r}_1 - \vec{r}_2|$ is not fulfilled.

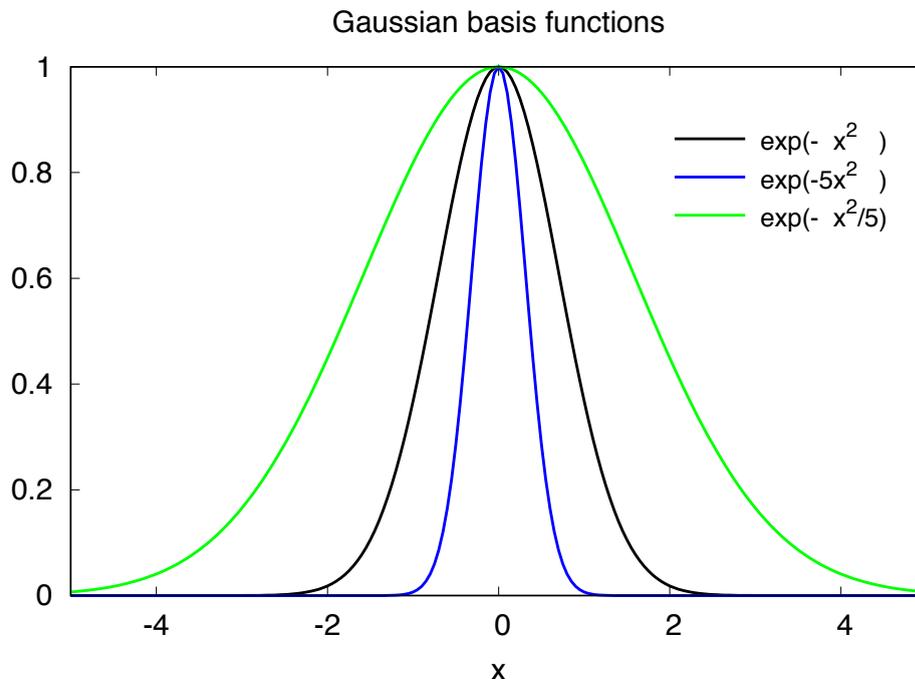


Fig. 4: Visualization of Gaussians: tight (blue, mainly relevant for the core region); diffuse (green, important for the region of the chemical bond).

Despite these formal disadvantages of Gaussians, they have become dominant in the field of molecular quantum chemistry.

The value of the exponent ζ determines whether the Gaussian function is called tight (roughly those with $\zeta \gg 1$) or diffuse (roughly: $\zeta \ll 1$ in atomic units). Tight functions are more relevant to describe the core region, whereas diffuse functions are more relevant for the chemical bond (see figure 4).

For efficiency reasons, several primitive Gaussians may be combined into a contracted Gaussian with fixed contraction coefficients d_i

$$\phi(\vec{r}-\vec{A}) = N (x-A_x)^a (y-A_y)^b (z-A_z)^c \sum_{i=1}^L d_i \exp(-\zeta_i(\vec{r}-\vec{A})^2) \quad (37)$$

This is usually done for tight exponents: if the contraction coefficients d_i were allowed to be optimized, then they would not change very much from system to system, as the tight functions mainly describe the core region close to the cusp at the nuclear position. It is thus more efficient to optimize the contraction coefficients d_i once for a given atom, and then keep them fixed. The molecular orbitals are then expanded as shown in equation (18).

In a similar way, crystalline orbitals for periodic systems may be obtained. First, basis functions are constructed which satisfy the Bloch condition for electrons in a periodic potential

$$\Phi_\mu(\vec{r}, \vec{k}) = \sum_{\vec{g}} \phi_\mu(\vec{r}-\vec{A}_\mu-\vec{g}) \exp(i\vec{k}\vec{g}) \quad (38)$$

where the summation is over the direct lattice vectors \vec{g} , and the basis functions now depend on the reciprocal lattice vector \vec{k} . Analogous to molecular orbitals, equation (18), crystalline

orbitals are expressed as

$$\Psi_i(\vec{r}, \vec{k}) = \sum_{\nu} c_{\nu i}(\vec{k}) \Phi_{\nu}(\vec{r}, \vec{k}). \quad (39)$$

Angular part

The angular part is obtained by multiplying a spherical harmonic $Y_{lm}(\vartheta, \varphi)$ with a factor the r^l which leads to the solid harmonics

$$r^l Y_{lm}(\vartheta, \varphi) \quad (40)$$

which are the solutions of the Laplace equation $\nabla^2 \phi(\vec{r}) = 0$ that are regular at the origin, being (orthogonal) polynomials in the coordinates x , y , and z of degree l .

The solid harmonics are in general complex. However, only in the case of atoms and linear molecules, L_z is a good quantum number. Therefore, real solid harmonics are usually used [2] by taking the real or imaginary part of the complex solid harmonics, mixing quantum numbers m and $-m$, as this reduces the computational effort.

Examples are (normalization is ignored):

$$\begin{aligned} l = 0 : \quad Y_{00} &\Rightarrow \sim 1 \\ \\ l = 1 : \quad r(Y_{11} - Y_{1-1}) &\Rightarrow \sim x \\ \quad r(Y_{11} + Y_{1-1}) &\Rightarrow \sim y \\ \quad rY_{10} &\Rightarrow \sim z \\ \\ l = 2 : \quad r^2 Y_{20} &\Rightarrow \sim 3z^2 - r^2 = 2z^2 - x^2 - y^2 \\ \quad r^2(Y_{21} - Y_{2-1}) &\Rightarrow \sim xz \\ \quad r^2(Y_{21} + Y_{2-1}) &\Rightarrow \sim yz \\ \quad r^2(Y_{22} + Y_{2-2}) &\Rightarrow \sim x^2 - y^2 \\ \quad r^2(Y_{22} - Y_{2-2}) &\Rightarrow \sim xy \end{aligned} \quad (41)$$

Some codes work with the five d functions as listed in equation (41), whereas others work with six Cartesian d functions ($x^2, y^2, z^2, xy, xz, yz$). The latter choice seems at first glance in contradiction to quantum mechanics as there are only five d functions. This can however be explained as there is a combination $x^2 + y^2 + z^2$ which is s -like and corresponds to a function $r^2 \exp(-\zeta r^2)$. The choice of six d functions thus leads to a larger basis set and usually a lower energy compared to the case of five d function. Some codes offer the option to switch between five and six d functions (and correspondingly seven or ten f functions).

The order in which the functions are implemented depends on the code. It is important to know this order for population analyses or projected densities of states; or to understand occupancies of orbitals, e.g., in the presence of crystal field splitting.

Choice of basis sets

Even tempered basis sets

A simple yet good choice for the basis set is to use even tempered exponents [12]. A set of exponents ζ is obtained according to the formula

$$\zeta_k = \alpha\beta^k \quad (42)$$

with the parameters α and β to be optimized, $k = 1, \dots, M$. This has been done in [12] for the atoms in the first three periods. It turned out that β should be in the range from 2...4.

Databases

For molecular calculations, large databases exist, especially (web addresses last accessed on June 7, 2021):

- the basis set database of the Environmental Molecular Sciences Laboratory (EMSL) employing the basis set exchange software [13, 14] at www.basissetexchange.org
- the basis set library of the Molpro [15] code at www.molpro.net/info/basis.php?portal=user&choice=Basis+library
- for periodic systems, the basis set library of the CRYSTAL [16] code at www.crystal.unito.it/basis-sets.php

Some notions: double zeta and similar, polarization functions

The smallest possible choice would be a minimal basis set (see section 3) which is, however, a poor choice. It lacks flexibility when, e.g., a chemical bond is formed. Such basis sets are rarely chosen. An exception may be embedding, when some atoms far away from the interesting region need to be described in a very efficient way.

A better choice would be to have two basis functions per orbitals, which is called a double-zeta basis set. This may be further extended to triple-, quadruple-, ... zeta basis sets.

As the inner orbitals change less when a molecular bond is formed so that they can be well described by a contracted Gaussian, a standard choice is to use more basis functions which mainly describe the valence shell. Normally, at least two basis functions for the valence shells should be used, which corresponds to a valence double zeta basis set.

When a free atom gets exposed to an electric field, or when a second atom is introduced and a chemical bond is formed, then the electronic charge distribution will not be radially symmetric any more. To be able to describe this, polarization functions are necessary. For example, for a hydrogen atom in its ground state, s -functions would be sufficient. To describe polarization, at least p -functions are required. This is visualized in figure 5.

A valence double-zeta plus polarization function basis may already be a good starting point for Hartree-Fock or DFT calculations. For wave function based correlation, it is important

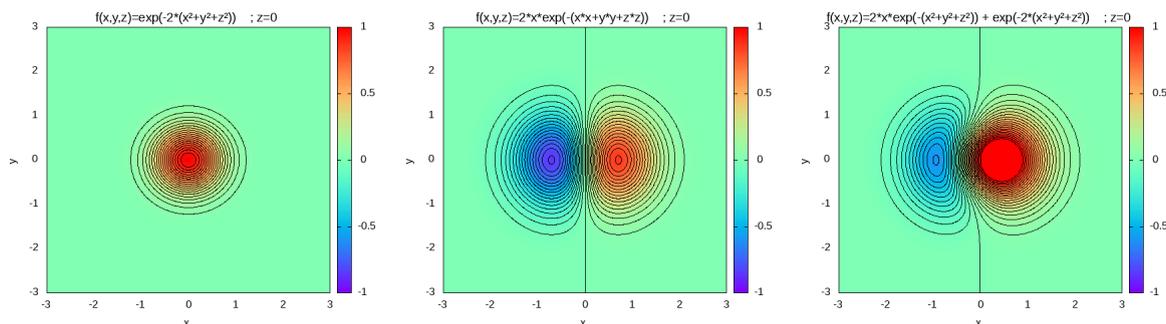


Fig. 5: An *s* function, which is always spherically symmetric (left); a *p* function in order to polarize the charge distribution (middle); and the two function added together, e.g. in response to an electric field (right).

that excitations to unoccupied orbitals can be described. This requires in general much larger basis sets, with higher angular momenta and extra diffuse functions. A hierarchy of correlation-consistent basis sets has been developed and is continuously extended [17].

Recommendations

Various issues have to be considered when choosing the basis set:

- The basis set depends on the charge state of the atom. Negative ions have a larger radius than positive ions and thus require diffuse exponents (e.g. oxygen usually needs extra diffuse functions).
- Wave function based correlation calculations need (significantly) larger basis sets compared to Hartree-Fock or DFT calculations.
- Polarisation functions should usually be included.
- Different properties may require enlarged basis sets, e.g., higher angular momenta when polarizabilities are computed, or extra tight functions for properties near or at the nucleus.
- Diffuse exponents are important for the describing chemical bonds.
- Effective core potentials may be advantageous from the first row of transition metals on.

To test a basis set, one may compare selected properties (total energy, band structure, equilibrium geometry) with an enhanced basis set. The Mulliken population is computationally practically without cost, and may thus always be computed; it gives the occupancies of the individual basis functions and thus a possibility to judge the importance of the various functions.

An enormous variety of basis sets has been generated, and the names are not systematic. A way of characterizing the basis set is to count the number of uncontracted and contracted basis functions, and then label the basis with a name such as

$$(10s4p)/[3s2p] \quad (43)$$

While this is not unambiguous, it gives an idea of the size and quality of the basis set.

7 Beyond Hartree-Fock: electron correlation

Up to now, the wave function based methods were restricted to using a single Slater determinant, i.e., the Hartree-Fock level. This however lacks electron correlation [18]: on the Hartree-Fock level, only the averaged position of the other electrons is considered; whereas the electrons interact with each other according to the actual position of the other electrons.

To describe this, more than one Slater determinant is required. Due to the variational principle, this will lower the energy: compared to the energy at the Hartree-Fock level, an additional contribution is obtained, the correlation energy. The correlation energy is only a small fraction of the total energy, and the computed energy thus changes by only a small amount. Nevertheless, the correlation energy is important to obtain correct values for energy differences, which affects, e.g., the binding energy, electron affinities, ionization potentials. In solids, the band gap depends strongly on electron correlation: band gaps on the Hartree-Fock level are usually largely overestimated, because, e.g., screening is not properly taken into account. As the correlation energy depends on the geometry, it will thus influence the equilibrium geometry.

Another fundamental problem of Hartree-Fock theory is that it gives a vanishing density of states for metals [19].

Despite these problems of the Hartree-Fock approach, it is nevertheless of enormous importance, for several reasons: it is a mathematically clear theory, without unknown parameters. Moreover, it can be systematically improved. Systematic and controlled approaches usually start from the Hartree-Fock level, and with these post-Hartree-Fock methods, high accuracy is achieved.

7.1 Second Quantization

To describe excitations from a Slater determinant, it is more convenient to use second quantization. Here, excitations are described with creation and annihilation operators. Instead of a Slater determinant

$$\Psi_{HF}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \cdots & \chi_i(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \cdots & \chi_i(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & & \vdots & & \vdots \\ \chi_1(\vec{x}_N) & \cdots & \chi_i(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (44)$$

we write

$$|\Psi_{HF}\rangle = a_1^\dagger \cdots a_i^\dagger \cdots a_N^\dagger |0\rangle.$$

a_i^\dagger and a_i are creation and annihilation operators for an electron in a molecular orbital i , with the anti-commutation relations

$$\{a_i^\dagger, a_j\} = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij} \quad \text{and} \quad \{a_i^\dagger, a_j^\dagger\} = \{a_i, a_j\} = 0$$

A determinant of an excited state, with electron excited from orbital i into orbital a

$$\Psi_i^a(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \cdots & \chi_a(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \cdots & \chi_a(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & & \vdots & & \vdots \\ \chi_1(\vec{x}_N) & \cdots & \chi_a(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (45)$$

can then be conveniently written in second quantization as

$$|\Psi_i^a\rangle = a_a^\dagger a_i |\Psi_{HF}\rangle.$$

Similarly, a two-fold excited state

$$\Psi_{ij}^{ab}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \cdots & \chi_a(\vec{x}_1) & \cdots & \chi_b(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \cdots & \chi_a(\vec{x}_2) & \cdots & \chi_b(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & & \vdots & & \vdots & & \vdots \\ \chi_1(\vec{x}_N) & \cdots & \chi_a(\vec{x}_N) & \cdots & \chi_b(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \quad (46)$$

becomes

$$|\Psi_{ij}^{ab}\rangle = a_b^\dagger a_a^\dagger a_i a_j |\Psi_{HF}\rangle.$$

Operators must have the same matrix elements in first and second quantization. This leads (see, e.g. [2]) to the mappings

$$H = H_1 + H_2 + H_{nn}$$

with the one-electron part of the Hamiltonian in second quantization being given by

$$H_1 = \sum_{pq} \langle \chi_p | h | \chi_q \rangle a_p^\dagger a_q$$

and the corresponding expression for the two-electron part

$$H_2 = \frac{1}{2} \sum_{pqrs} \left\langle \chi_p \chi_q \left| \frac{1}{r_{12}} \right| \chi_r \chi_s \right\rangle a_p^\dagger a_q^\dagger a_s a_r$$

where the sums over p, q, r, s run over all spin orbitals, while the nuclear-nuclear repulsion H_{nn} is, of course, just a number, determined by the positions of the nuclei and their charges.

7.2 Wave function based correlation

Full configuration interaction

A wave function based approach to include correlation can now be expressed by adding all possible excited determinants, which corresponds to full configuration interaction (full CI),

$$\Psi_{\text{full CI}} = \left(1 + \sum_i^a t_a^i a_a^\dagger a_i + \sum_{\substack{a < b \\ i < j}} t_{ab}^{ij} a_b^\dagger a_a^\dagger a_i a_j + \sum_{\substack{a < b < c \\ i < j < k}} t_{abc}^{ijk} a_c^\dagger a_b^\dagger a_a^\dagger a_i a_j a_k + \dots \right) |\Psi_{HF}\rangle = \sum_I c_I |\Psi_I\rangle.$$

The energy is obtained as

$$E_{\text{full CI}} = \frac{\langle \Psi_{\text{full CI}} | H | \Psi_{\text{full CI}} \rangle}{\langle \Psi_{\text{full CI}} | \Psi_{\text{full CI}} \rangle}.$$

This is normalized, variational, and size-consistent (see below). However, the computational effort is enormous, as a huge matrix has to be diagonalized in the end: From

$$H | \Psi_{\text{full CI}} \rangle = E | \Psi_{\text{full CI}} \rangle$$

it follows that for all Ψ_I , it must hold

$$\langle \Psi_I | H - E_{\text{full CI}} | \Psi_{\text{full CI}} \rangle = 0$$

This is an eigenvalue problem. The lowest eigenvalue corresponds to the ground state energy, and the higher eigenvalues correspond to energies of excited states. Due to the finite basis set, the energies are upper bounds of the exact eigen-energies of the corresponding Hamiltonian: $E_n^{\text{exact}} \leq E_n^{\text{full CI}}$.

A general strategy in a CI calculation is to keep the low lying orbitals, the core orbitals, doubly occupied. This reduces the number of determinants without a great loss in accuracy.

Configuration interaction with single and double substitutions: CI(SD)

As full configuration interaction is usually too demanding, a restriction to wave functions with single and double substitutions is made instead

$$| \Psi_{\text{CI(SD)}} \rangle = \left(1 + \sum_a^i t_a^i a_a^\dagger a_i + \sum_{\substack{a < b \\ i < j}} t_{ab}^{ij} a_b^\dagger a_a^\dagger a_i a_j \right) | \Psi_{\text{HF}} \rangle$$

and the energy is obtained as the expectation value

$$E_{\text{CI(SD)}} = \frac{\langle \Psi_{\text{CI(SD)}} | H | \Psi_{\text{CI(SD)}} \rangle}{\langle \Psi_{\text{CI(SD)}} | \Psi_{\text{CI(SD)}} \rangle}.$$

This is again normalized and variational, but it is not size-consistent, as illustrated in figure 6: When the energy of two helium atoms at a very large distance is computed, then it should be the sum of the energy of the individual atoms. In two separate CI(SD) calculations for the atoms, all excitations are considered. In a single CI(SD) calculation for the supersystem of both atoms, not all excitations are considered: states where 3 or 4 electrons are excited are not considered. The sum of the energy of two separate CI(SD) calculations will thus be lower than the energy of a single CI(SD) calculation for the whole system. Thus, CI(SD) suffers from the size-consistency problem. The argument obviously holds for any truncated CI method, which only includes a finite number of excitations.

Besides, there are pathological cases such as H_2 described by a restricted closed shell wave function. When the hydrogen atoms are pulled apart, this wave function does not allow the molecule to properly dissociate. In this case, Hartree-Fock is not size-consistent. We will, however, in the following, exclude these cases when discussing size-consistency.



Fig. 6: Two helium atoms at a large distance, to illustrate the size-consistency problem.

Coupled cluster

Because of the size-consistency problem, CI(SD) is not a popular method. Instead, coupled cluster methods based on an exponential ansatz are nowadays preferred

$$|\Psi_{CCSD}\rangle = \exp\left(\sum_a^i t_a^i a_a^\dagger a_i + \sum_{\substack{a < b \\ i < j}} t_{ab}^{ij} a_b^\dagger a_a^\dagger a_i a_j\right) |\Psi_{HF}\rangle = \exp(T) |\Psi_{HF}\rangle$$

The above ansatz is labeled CCSD, coupled cluster with single and double substitutions. Since the exponential ensures that arbitrary powers of single and double substitutions are included, the approach is size consistent.

In coupled cluster methods, intermediate normalization is used: $\langle \Psi_{HF} | \Psi_{CCSD} \rangle = 1$. From $H|\Psi_{CCSD}\rangle = E|\Psi_{CCSD}\rangle$, the energy and the coefficients (amplitudes) t_a^i, t_{ab}^{ij} are obtained

$$\begin{aligned} \langle \Psi_{HF} | H - E | \Psi_{CCSD} \rangle &= 0 \\ \langle \Psi_i^a | H - E | \Psi_{CCSD} \rangle &= 0 \\ \langle \Psi_{ij}^{ab} | H - E | \Psi_{CCSD} \rangle &= 0. \end{aligned}$$

The obtained coupled cluster energy is, however, not variational.

Møller-Plesset Perturbation theory, 2nd order: MP2

Perturbation theory is one of the methods frequently used to approximately solve the Schrödinger equation. It decomposes the full Hamiltonian H into an unperturbed part H_0 and the remaining part H_1 . Subsequently, the wave function and eigenvalues are expanded in a power series of a coupling parameter λ .

In MP2, the unperturbed Hamiltonian is chosen to be the Fock operator

$$H = H_0 + H_1 = \sum_{i=1}^N f(i) = \sum_{i=1}^N (h(i) + v_{HF}(i))$$

where $h(i)$ is the one-electron part, i.e., kinetic energy and nuclear attraction. The 0th order wave function is thus the Hartree-Fock Slater determinant, equation (7). The 0th order energy

is just the sum of the eigenvalues

$$E_0 = \sum_{i=1}^N \varepsilon_i.$$

The first order energy is obtained as the expectation value of the perturbation H_1

$$E_1 = \langle \Psi_0 | H_1 | \Psi_0 \rangle = \langle \Psi_0 | H - H_0 | \Psi_0 \rangle = E_{HF} - E_0.$$

The sum of zeroth and first order energies is thus just the Hartree-Fock energy

$$E_0 + E_1 = E_{HF}.$$

The perturbation can be written as

$$H_1 = \sum_{\substack{i,j=1 \\ i < j}}^N \frac{1}{r_{ij}} - \sum_{i=1}^N v_{HF}(i)$$

The second order correction is obtained as

$$E_{MP2} = - \sum_{a < b} \sum_{k < l} \frac{\iint d^3 r_1 d^3 r_2 \left(\frac{\chi_a^*(\vec{r}_1) \chi_k(\vec{r}_1) \chi_b^*(\vec{r}_2) \chi_l(\vec{r}_2) - \chi_a^*(\vec{r}_1) \chi_l(\vec{r}_1) \chi_b^*(\vec{r}_2) \chi_k(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \right)^2}{\varepsilon_a + \varepsilon_b - \varepsilon_k - \varepsilon_l}$$

where a and b refer to unoccupied orbitals, k and l to occupied ones.

MP2 is size-consistent, but not variational. Compared to CI(SD) or CCSD, MP2 is computationally cheap.

7.2.1 Multi-configuration SCF (MCSCF)

In the case of (near-)degeneracies or low-lying excited states (usually occurring in strongly correlated systems), multi-configuration self-consistent field calculations may be a remedy. Here, a set of Slater determinants is used instead of just one

$$|\Psi_{MCSCF}\rangle = \sum_I C_I |\Psi_I\rangle.$$

The Slater determinants are from an active space

$$|\Psi_I\rangle \in \{c_0 |\Psi_{HF}\rangle, c_a^k |\Psi_k^a\rangle, c_{ab}^{kl} |\Psi_{kl}^{ab}\rangle, c_{abc}^{klm} |\Psi_{klm}^{abc}\rangle, \dots\}.$$

The coefficients c and some of the orbitals are optimized.

The active space and which orbitals are optimized is left to the user of the code, but determine the computational effort. MCSCF is good to treat static correlation effects, where static correlation means correlation due to (near-)degeneracies.

Electron correlation due to the Coulomb repulsion is in contrast called dynamical correlation. To describe dynamical correlation, excitations to many virtual orbitals are necessary, which is better done with configuration interaction.

Besides systems with low-lying excited states, MCSCF can also be used in the aforementioned case of the dissociation of H_2 . With an MCSCF ansatz, two hydrogen atoms at large distance can be well described, and size-consistency achieved. Another example is the proper description of oxygen in its ground state: the p -occupancy is $2p^4$. A single Slater determinant with, e.g., an occupancy of $p_x^2 p_y p_z$ would break the spherical symmetry. Such a wave function is not an eigenstate of L^2 . To restore symmetry, a state-averaged calculation with 3 determinants ($p_x^2 p_y p_z, p_x p_y^2 p_z, p_x p_y p_z^2$) is performed in MCSCF.

MCSCF alone does usually not recover a large fraction of the correlation energy, as this would require an enormous active space. It is, however, able to provide better starting orbitals for a subsequent CI calculation.

Multi-reference configuration interaction (MRCI)

A powerful tool in these situations is to follow a multi-configuration self-consistent field calculation with a configuration interaction calculation, which is multi-reference CI

$$|\Psi_{MRCI(SD)}\rangle = \left(1 + \sum_{ai} t_a^i a_a^\dagger a_i + \sum_{abij} t_{ab}^{ij} a_b^\dagger a_a^\dagger a_i a_j \right) |\Psi_{MCSCF}\rangle$$

where the coefficients t are optimized.

Explicit correlation: F12

To take the electronic cusp condition (equation (36)) into account, explicit correlation has been introduced by multiplying the wave function with a factor such as

$$\left(1 - \frac{1}{\gamma} \exp(-\gamma|\vec{r}_1 - \vec{r}_2|) \right)$$

This makes accurate calculations possible which would otherwise require very large basis sets. This is similar to Jastrow factors in quantum Monte Carlo. Explicit correlation was pioneered by Hylleraas [20] in his treatment of the He atom, where he introduced an ansatz for the wave-function depending on the distance $|\vec{r}_1 - \vec{r}_2|$.

Local correlation schemes

Local correlation methods have become popular, to reduce the computational effort, and make schemes such as coupled cluster available for extended systems. One variant is based on pair natural orbitals [21]. Also, the treatment of correlation in periodic systems has been targeted with local methods, e.g., the incremental scheme [22,23].

8 Properties

After computing the total energy, calculating other properties is particularly interesting, as usually a comparison with the experiment can be made. The global minimum of the total energy as

a function of geometrical parameters gives the equilibrium geometry. Here, the first derivative of the energy with respect to nuclear positions is of great use. At the global minimum, second derivatives with respect to nuclear positions give the vibrational spectrum. Further derivatives are extremely useful, e.g., infrared intensities may be expressed as second derivatives, one derivative with respect to nuclear positions and one with respect to an external electric field, or Raman intensities as third derivatives, one derivative with respect to nuclear positions and two with respect to an external electric field.

As a whole, measurable properties may be expressed as derivatives with respect to electric field \vec{F} , magnetic field \vec{B} , nuclear magnetic moment \vec{I} , electron magnetic moment \vec{s} , or nuclear position \vec{R} , in such a way (see also the overview given in [3])

$$\frac{\partial^{n_F+n_B+n_I+n_s+n_R} E}{\partial \vec{F}^{n_F} \partial \vec{B}^{n_B} \partial \vec{I}^{n_I} \partial \vec{s}^{n_s} \partial \vec{R}^{n_R}}.$$

These derivatives may be obtained analytically or numerically. Analytical gradients are often difficult to implement; however, once they are available, they are advantageous, as they are faster and have less numerical noise.

9 Examples

Oxygen electron affinity

A challenging example is the calculation of the electron affinity of oxygen shown in table 1. High-level correlation calculations with extended basis sets are required to achieve good agreement with the experiment. Including triples perturbatively (marked with (T)) is important to get close to the experimental value.

Note that on the Hartree-Fock level, even the sign is wrong. Importantly, the orbital eigenvalues of the occupied orbitals are negative which makes the calculation meaningful. This is in general not the case for density functional calculations: many functionals suffer from the drawback that the eigenvalues of occupied orbitals may be positive when an atom is negatively charged [24, 25]. Negative ions would be instable in such a case of positive orbital eigenvalues.

A similar comparison (various properties such as geometries, atomization energies, reaction enthalpies) for a set of molecules can be found in [2].

Table 1: Computed (with Molpro [15] and MCHF [26]) electron affinity of oxygen (in eV). The experimental value is 1.461 eV.

basis set	method					
	HF	CI(SD)	CCSD	CCSD(T)	CCSD-F12	CCSD(T)-F12
aug-cc-pvdz	-0.493	0.941	1.086	1.188	1.294	1.394
aug-cc-pvtz	-0.525	1.016	1.185	1.335	1.299	1.445
aug-cc-pvqz-f12	-0.534	1.068	1.245	1.410	1.303	1.465
aug-cc-pv5z-f12	-0.535	1.084	1.264	1.431	1.298	1.464
numerical (MCHF)	-0.535					

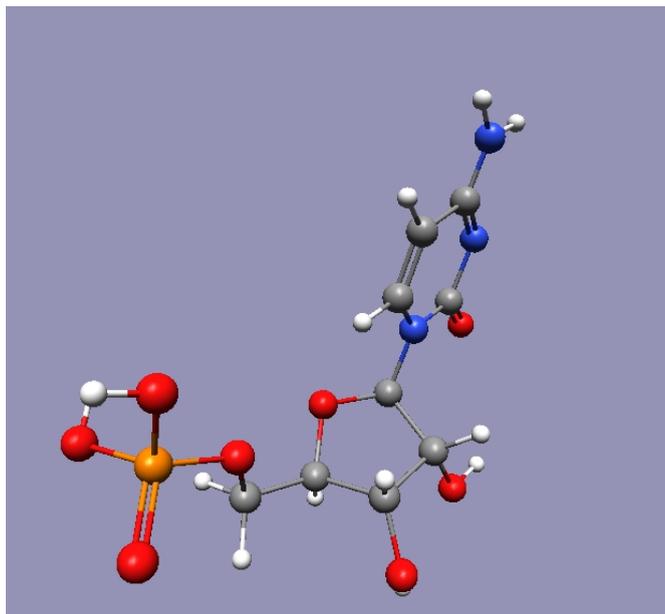


Fig. 7: The molecule cytidine monophosphate; 35 atoms, 835 basis functions, PNO-LCCSD(T).

Local correlation calculation

An example of today's state of the art is shown in figure 7. The molecule cytidine monophosphate (35 atoms, 168 electrons in total, 118 electrons correlated) is calculated at the level of PNO-LCCSD(T), with a cc-pV(T+d)Z basis set (835 contractions). PNO-LCCSD(T) means that pair natural orbitals are used for the correlation calculation, which is local coupled cluster (singles, doubles are fully, and triples perturbatively taken into account). The energy calculation with Molpro [15] takes about 174 minutes on 12 cores. For comparison, a traditional CCSD calculation would not be feasible, or require enormous CPU time.

Superexchange calculation

In the field of strong correlation, the *ab initio* calculation of magnetic coupling parameters is a challenging task. NiO is a prototype example. Here, two next-nearest neighboring Ni atoms couple antiferromagnetically via an oxygen atom (figure 8).

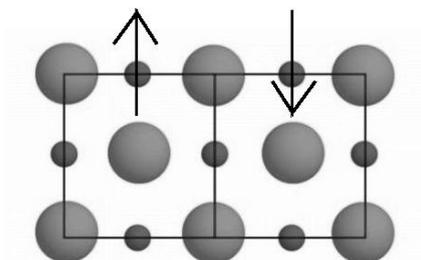


Fig. 8: NiO: two nickel spins are marked with arrows. They couple antiferromagnetically via the oxygen atom in between.

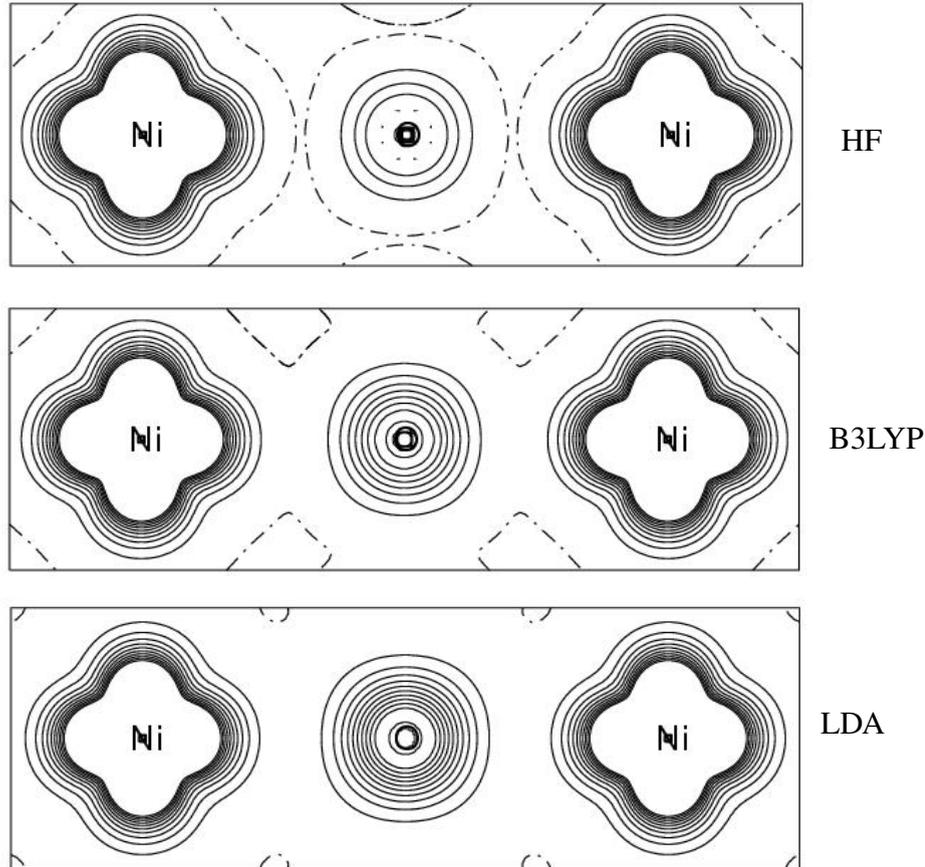


Fig. 9: *NiO*: spin densities in the ferromagnetic state, at the level of Hartree-Fock (top), B3LYP (middle), LDA (bottom). The same values of the contour lines are used in the three plots.

Exchange couplings may be computed by calculating the energies of the ferromagnetic state and the antiferromagnetic state, and then fitting to a model Hamiltonian such as the Ising or Heisenberg model. The energy difference ΔE will then be proportional to the number of neighbors z (i.e. the number of couplings), the spins on the two sites (S_1, S_2), and the exchange coupling J , here $\Delta E \sim zJS^2$ for the Ising model. This can be compared with experimental values for the Néel temperature.

Spin densities at the level of Hartree-Fock, the local density approximation (LDA), and the hybrid functional B3LYP are shown in figure 9. To emphasize the differences, the spin densities are shown for the ferromagnetic state.

Hartree-Fock theory leads to a rather localized spin density which is shown at the top of figure 9. The computed Ni magnetic moment is about $1.9 \mu_B$. LDA shows a much more delocalized spin density, with a Ni magnetic moment of $1.6 \mu_B$. The hybrid functional B3LYP which has admixtures of Hartree-Fock and LDA is somewhere in between, with $1.8 \mu_B$.

Due to the more delocalized spin density in B3LYP, and even more so in LDA, exchange couplings are much larger in magnitude. The computed superexchange value ranges from -5.4 meV (Hartree-Fock) and -29 meV (B3LYP) to -94 meV (LDA). This is thus an example where Hartree-Fock severely deviates due to the lack of correlation, and density functional theory produces results varying over a very wide range.

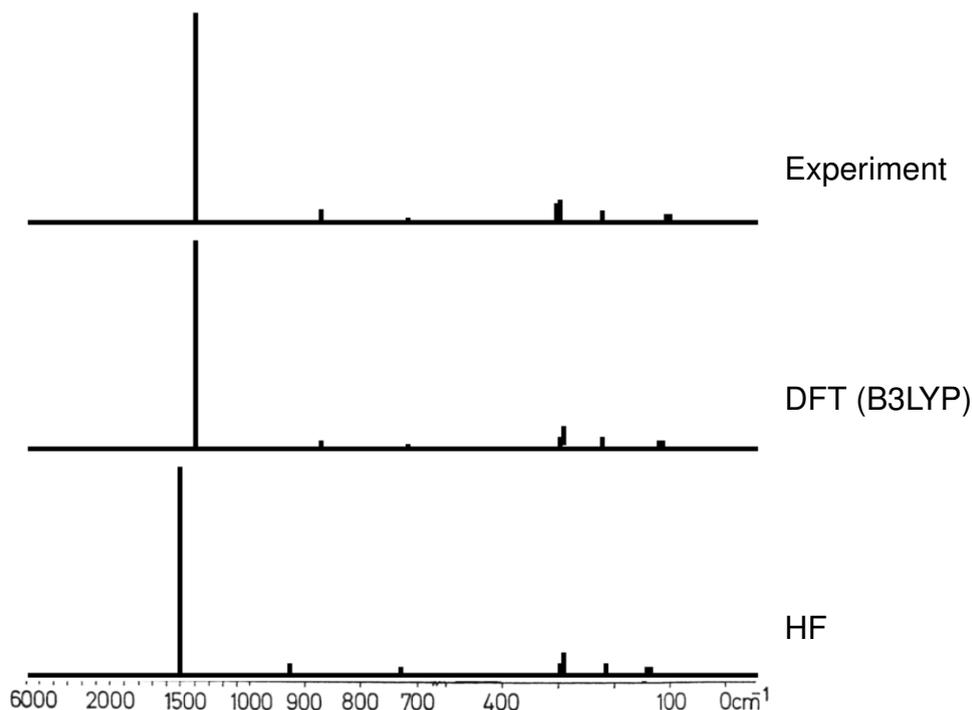


Fig. 10: *The infrared spectrum of calcite: experimental (top), DFT with B3LYP (middle), Hartree-Fock (bottom).*

A controlled approach is possible by using a cluster and embedding it, to model the bulk. This way, calculations with molecular codes become feasible, and wave function based methods such as CASPT2 may be used. This gives better agreement with experiment (-20 meV), with CASPT2 values in the range of about from -14 to -17 meV [27,28].

Vibrational spectroscopy

We finish with another example from the solid state, is displayed in figure 10, computed with CRYSTAL [16]. The infrared spectrum of calcite (CaCO_3) [29] matches the experiment [30] excellent at the DFT level, with the hybrid functional B3LYP. At the Hartree-Fock level, the agreement is less good, but still reasonable.

In general, geometries usually agree well with experiment in DFT. Vibrational frequencies deviate a bit more, but are still in good agreement with experiment. Also, IR and Raman intensities usually agree well. As wave function based correlation is not available for IR or Raman spectra of solids, it is state of the art to employ DFT. It is recommended to compare various functionals to have a band width of results. E.g., here and for many other materials, B3LYP works excellent, but there are exceptions such as the narrow band gap insulator FeSi where B3LYP strongly deviates from experiment, and even a simple LDA calculation performs much better. Calculated vibrational spectra have become a powerful tool, and computed IR and Raman spectra are now often used to complement experimental results.

10 Conclusion

Quantum chemical methods have gained enormously in importance in recent years, and their use has become more widespread. This is, on the one hand, due to the growth in computational resources. On the other hand, even traditional methods such as Hartree-Fock have been made significantly more efficient due to approximations in the integral calculation with density fitting. Also, new highly efficient methods to treat wave function based correlation have been introduced.

Programs have become user-friendly so that they may be handled by a broad community. Numerous properties may be computed, which has attracted great interest from experimentalists also, e.g., for infrared, Raman, and NMR spectroscopy. The codes have also grown enormously in size and complexity. Still, wave function based correlation, especially for periodic systems, remains one of the key challenges.

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