Self-consistent procedure to solve the Kohn-Sham equations

We recall now the self-consistent procedure to solve Kohn-Sham equations. Once a suitable approximation for the unknown functional \( E_{xc}[\rho] \) is chosen, the corresponding exchange-correlation potential \( v_{xc}\{\rho(r)\} \) can be derived analytically and the solution of the Kohn-Sham equations proceeds by the following self-consistent cycle.

- **A**: choosing the \textbf{initial set of Kohn-Sham orbitals} \( \psi_j^0 \);
- **B**: calculation of the \textbf{electron density} \( \rho^0 = \sum_{i=1}^{N} |\psi_i^0|^2 \);
- **C**: calculation of the \textbf{Kohn-Sham effective potential} \( v_{eff}\{\rho^0(r)\} \);
- **D**: solving the \( \left[ -\frac{1}{2} \nabla^2 + v_{eff} \right] \psi^d_j = \epsilon^d_j \psi^d_j \) equation
  (for instance, representing \( \psi^d_j \) as a linear combination of basis set functions \( \{\chi_k\} \), diagonalization of the \( \langle \chi_i^0 | -\frac{1}{2} \nabla^2 + v_{eff} | \chi_j^0 \rangle \) matrix the eigenvectors form a new set one-electron functions \( \psi^d_j \));
- **E**: \textbf{convergency check};
  - positive then \textbf{terminate};
  - negative then \textbf{replace} \( \psi_j^0 \) \textbf{by} \( \psi^d_j \) \textbf{and go to} B;
- **F**: \textbf{termination}:
  calculation of the final energy and other properties;
Basis sets

The solutions $\psi_j^0$ are represented as linear combinations of simpler functions forming a **basis set**:

$$\psi_j^0 = \sum_{k=1}^{M} C_{jk} \chi_k(r)$$

The coefficients $C_{jk}$ can be obtained from the following secular equation (Note the similarity to the Hartree-Fock-Roothaan equations):

$$\sum_{\mu=1}^{M} \left[ F_{\nu \mu} - \epsilon_i S_{\nu \mu} \right] C_{\mu i} = 0 \quad \nu = 1, M$$

where $M$ denotes the number of the basis functions $\chi_k$ and the matrix $F_{\mu \nu}$ equals:

$$F_{\mu \nu} = \left( \chi_\mu \left| -\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r' - r|} dr' + v_{xc}(\rho(r)) \right| \chi_\nu \right)$$

Different types of **basis sets** are used in quantum chemistry, such as:

- **Gaussian Type Functions (GTO):** The radial part of each basis set function is a linear combination of 'primitive gaussians' of the following form:

$$\phi(x, y, z; \alpha, i, j, k) = \left( \frac{2\alpha}{\pi} \right)^{3/4} \left[ \frac{(8\alpha)^{i+j+k} i! j! k!}{(2i!) (2j!) (2k!)} \right]^{1/2} x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)}$$
where \( \mathbf{r}_o \) is usually the position of the nucleus on which this function is localized. The angular part is described using real functions of the corresponding symmetry: three functions for \( p \)-orbitals \((x, y, z)\), five (or six) functions for \( d \) orbitals \((xx, yy, zz, xy, x^2 - y^2)\), etc.

Gaussian basis sets are **widely used** in quantum chemistry. They are used also in the program Gaussian98. In the Kohn-Sham calculations, the same basis sets are used as the ones developed for wave-function based approaches (STO-3G, 3-21G, 6-31G, 6-31G*, 6-31G**, 6-311G, 6-311G+G(d,p), 6-311G+G(2d,p),...,

So-called *correlation consistent* basis sets provide probably the most systematic series of GTO basis sets of increasing quality\(^1\). The following *correlation consistent* basis sets are in use:

- **cc-pVDZ**: valence double zeta:
  
  \((2s,1p)\) for H, \((3s,2p,1d)\) for B-Ne, \((4s,3p,1d)\) for Al-Ar,

- **cc-pVTZ**: valence triple zeta:
  
  \((3s,2p,1d)\) for H, \((4s,3p,2d,1f)\) for B-Ne, \((5s,4p,3d,1f)\) for Al-Ar,

- **cc-pVQZ**: valence quadruple zeta:
  
  \((4s,3p,2d,1f)\) for H, \((5s,4p,3d,2f,1g)\) for B-Ne, \((6s,5p,3d,2f,1g)\) for Al-Ar,

- **cc-pV5Z**: valence quintuple zeta:
  
  \((5s,4p,3d,2f,1g)\) for H, \((6s,5p,4d,3f,2g,1h)\) for B-Ne, \((7s,6p,4d,3f,2g,1h)\) for Al-Ar.

function of each type $s$, $p$, $f$, $g$, $h$, etc. The corresponding labels for such functions are: $AUG$-$cc$-$pVDZ$, $AUG$-$cc$-$pVTZ$, $AUG$-$cc$-$pVQZ$, and $AUG$-$cc$-$pV5Z$.

Also functions especially designed for Kohn-Sham calculations are used (for instance, the basis sets developed in Montreal by Salahub and collaborators $^2$).

- **Slater Type Functions (STO):** The basis set functions represent the main features of the atomic orbitals, i.e. the exponential radial behaviour, and the derivative discontinuity at the nucleus (Recall Kato’s condition introduced earlier in this course!):

\[
\exp[-\alpha |\mathbf{r} - \mathbf{r}_o|]
\]

The exponential part is multiplied by a prefactor of a general form:

\[
r^k r x^k x y^k y z^k z
\]

This type of functions are applied in the program ADF. For recently developed series of STO’s of increasing quality developed by D. Chong see Ref. $^3$.

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• **Plane-waves:** The functions of the form:

\[
\exp[-i \mathbf{k} \cdot \mathbf{r}]
\]

For a periodic system, such functions form a complete set. The higher number of planewaves is used the more complete is the basis set. The highest value of the \(|\mathbf{k}|\) which is a **single number** determines, therefore, the quality of the used basis set. This is a very simple criterion compared to the criteria used to classify the basis sets comprising localized functions. The plane-waves are usually applied in modeling the condensed matter (solids, liquids, surfaces) by means of such methods as Car-Parrinello simulations. Plane-waves are less frequently used in calculations for isolated molecules. In such a case, the studied molecule is placed in a periodic **supercell** of a sufficiently large size.

• **Other:** For instance, numerical basis sets, augmented plane-waves, special functions (Bessel).
Basis Set Superposition Error

Using finite basis sets involves inevitably the basis set completeness problem. Similarly as in the wave-functions based approaches, the solution of the Kohn-Sham equations depends on the basis set used. Numerical evidence shows that the convergence of the results with the increase of the number of gaussian type functions is similar in the Kohn-Sham and the Hartree-Fock approaches.

To obtain the interaction energies using the supermolecule Kohn-Sham calculations the effect of the incompleteness of the basis set can be estimated using the counterpoise technique proposed by Boys and Bernardi \(^4\). This technique has been widely applied combined with other computational methods of quantum chemistry.

According to the counterpoise technique, the interaction energy in a complex \(A \cdots B\) \((E_{\text{int}}^{AB})\) is calculated as:

\[
E_{\text{int}}^{AB} = E^{AB} - E^{(A)B} - E^{A(B)}
\]

where \(E^{A(B)}\) denotes the energy of the molecule A calculated with all the basis set functions available in the complex, including the orbitals localized on the molecule B.

Obtaining the elements of the secular equation

Each term of $F_{\mu\nu}$ is treated in a different way:

- **The kinetic energy:**
  $\left( \chi_\mu \left| -\frac{1}{2} \nabla^2 \right| \chi_\nu \right)$

  This term can be obtained in the same way as it is calculated in the Hartree-Fock method. In particular, this term can be expressed analytically if gaussian type functions are used.

- **The external potential term:**
  $\left( \chi_\mu \left| v(r) \right| \chi_\nu \right)$

  For atoms and molecules this component takes the form of the sum of nuclear attraction terms:

  $v(r) = -\sum A Z_A \frac{1}{|R_A - r|}$

  $v(r)$ can also contain a part due to the interaction with external electric field.

  This term can be obtained in the same way as it is calculated in the Hartree-Fock method. In particular, this term can be expressed analytically if gaussian type functions are used.

- **The Coulomb term:**
  $\left( \chi_\mu \left| \int \frac{\rho(r')}{|r' - r|} dr' \right| \chi_\nu \right)$

  This term can be obtained in the same way as it is calculated in the Hartree-Fock method. In particular, this term can be expressed analytically if gaussian type functions are used. However,
this term is calculated not exactly but it is accurately approximated in most DFT programs (see later).

• The **exchange-correlation** term:

\[
(\chi_\mu | v_{xc}(\rho(\mathbf{r}))| \chi_\nu)
\]

Even for the Dirac’s exchange energy \( v_{xc} = -C_x^4 \rho^{1/3} \) which is the simplest functional in DFT this term can not be expressed analytically. **Numerical integration** is needed for this term.

• The **overlap integral** \( S_{\mu\nu} \):

\[
(\chi_\mu | \chi_\nu)
\]

Depending on the used basis set, this can can be calculated analytically or can be obtained through numerical integration.