Correlations

Explicitly included at the mean-field level:

- Statistics (fermions)
- Pairing (BCS or HFB)
- Deformation (can bring up to 20 MeV!)

Absent:

- Symmetry restoration
- Configuration mixing (shape, multi qp excitations, …)

Can all missing correlations be included in the interaction?
(“DFT spirit”)
Beyond mean-field

Set of mean-field wave functions depending on axial $q$

- Projection on $N$, $Z$, $J$:
  \[ |J0q\rangle = \frac{1}{N_{J0q}} \hat{P}_J \hat{P}_Z \hat{P}_N |q\rangle, \]

- New wave functions by mixing on $q$:
  \[ |J0k\rangle = \sum_q f_{J,k}(q) |J0q\rangle \]

with $f_{J,k}(q)$ determined by minimizing the energy:

\[ E_{J,k} = \frac{\langle J0k|\hat{H}|J0k\rangle}{\langle J0k|J0k\rangle} \]
Mean field projected on $J=0$

Bars in red: $0^+$ states obtained after configuration mixing
Collective wave functions
Hartree-Fock + BCS (Skyrme SLy6 interaction + density dependent zero-range pairing force) $\Rightarrow$ configuration mixing of angular-momentum and particle-number projected self-consistent mean field states

(M. Bender, P. Bonche, T. Duguet, and P.H. Heenen, PRC 69, 2004, 064303)
Pb isotopic shifts

FIG. 3: Difference from the experimental mean square charge radii (Expt), the beyond mean field calculations with normal [4] (MF) and decreased pairing [18] (MF*) and the IBM calculations (IBM) to the droplet model calculations for a spherical nucleus. Iso-deformation lines from the droplet model at $\beta_2=0.1$ and 0.15 are shown.
Global calculations
Projection + Configuration mixing for all e-e nuclei

Correlations due to - symmetry restorations
- configuration mixing
Density functional method

- Beyond mean-field: correlations introduced explicitly
- Why not implicitly in the interaction?
- How to fit an interaction?
- Existing tool: the density functional theory

- What do we want to be able to calculate:
  ground state properties only?
  spectra, transition probabilities, … also?

J. Perdew and S. Kurth, LNP 620, 1 (2003), Springer Verlag
Starting point of the DFT ideas: analysis of the Hartree-Fock method

(clarifying case: atoms and Coulomb interaction)

HF equations written as a function of the one-body diagonal and non diagonal densities:

\[ n(r) = \sum_j |\phi_j(r)|^2 \]

\[ n^{(1)}(r, r') = \sum_j \phi_j^*(r') \phi_j(r) \]
The HF equation:

\[
\varepsilon_k \phi_k(r) = \left( -\frac{\hbar^2}{2m} \Delta + v_{ext}(r) \right) \phi_k(r) + u(r) \phi_k(r) \\
- \int d^3r' n^{(1)}(r, r') v(r' - r) \phi_k(r')
\]

where \( u(r) = \int d^3r' v(r' - r) n(r') \)

The first line is easy: problem in a potential.
The second line is complicate: non local exchange term.
Moreover, correlations beyond a Slater determinant are missing.

But do we need all the information of the true gs wave function?

DFT: take full benefit of the form of the energy as a function of densities
simplify the exchange term
introduce what is missing from a mean-field model
Hohenberg Kohn theorem

Hamiltonian separated in two parts: $H_0$ (electron coordinates) (kinetic + 2-body)

$V_{\text{ext}}$ (external field, nucleus-electron)

Ground state wave function $\Psi$ gives the gs energy:

$$E = \langle \Psi | H_0 + V_{\text{ext}} | \Psi \rangle$$

and the density $n(r)$

density $\leftrightarrow$ energy $\leftrightarrow$ ground state wave function

(non degenerate)
Ground state wf minimizes $H$ over all antisymmetrised N-particle wf’s.

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

Two steps:
1. minimizing with respect to all the $\Psi$ giving the same density $n(r)$

$$\min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3r \, v(r)n(r)$$

All wave functions corresponding to the same density give the same matrix element for $v(r)$!

One defines the universal functional of the density:

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_{n}^{\text{min}} | \hat{T} + \hat{V}_{ee} | \Psi_{n}^{\text{min}} \rangle$$

$\Psi_{n}^{\text{min}}$ is the wave function corresponding to the minimum for a given $n$.
2. Minimization of the energy with respect to all N-electron densities

\[ E = \min_n E_v[n] \]

\[ = \min_n \left\{ F[n] + \int d^3r \; v(r)n(r) \right\} \]

Constraint on the number of particles N by a Lagrange multiplier \( \mu \)

\[ \delta \left\{ F[n] + \int d^3r \; v(r)n(r) - \mu \int d^3r \; n(r) \right\} = 0 \]

equivalent to:

\[ \frac{\delta F}{\delta n(r)} + v(r) = \mu \]
**Definition:**

the exchange-correlation energy $E_{xc}[n]$ is defined by

$$F[n] = T_s[n] + U[n] + E_{xc}[n]$$

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r - r'|}$$

The energy is given by:

$$E = T_s[n] + \int v(\vec{r})n(\vec{r}) d\vec{r} + U[n] + E_{xc}[n]$$

The density is determined through the Kohn Sham equation:

$$\left(-\frac{\hbar^2}{2m} \Delta + u([n]; \vec{r}) + v_{xc}([n]; \vec{r}')\right) \psi_\alpha(\vec{r}') = \epsilon_\alpha \psi_\alpha(\vec{r}')$$

which is a fictitious one-electron Shrödinger equation.
• The kinetic energy is treated exactly: large term responsible for density oscillations

The exchange correlation energy is approximated

• Two terms:

\[ E_{xc}[n] = E_x[n] + E_c[n] \]

where:

\[ E_x[n] = \langle \phi_n^{\min} | V_{ee} | \phi_n^{\min} \rangle = -U[n] \]

If \( \Phi_n^{\min} \) is a Slater, \( E_x \) is the Fock term of the KS orbital

Not HF term because \( \Phi_n^{\min} \) differs from the true HF orbital of the system

The correlation energy is well defined:

\[ E_c[n] = F[n] - \{ T_s[n] + U[n] + E_x[n] \} \]
Prescriptions to design a DFT

• Construction by “constraint satisfaction”: DFT must satisfy as many known exact constraints as possible
• Correct in the uniform density limit
• Scaling properties
• Correct long range part
• Avoid divergences caused by the approximation of the exchange energy (should the exchange be calculated exactly?)
• Self interaction problem
• No need that KS determinant display all symmetries of the true wave function.
Table 1.1. Typical errors for atoms, molecules, and solids from selfconsistent Kohn-Sham calculations within the LSD and GGA approximations of (1.11) and (1.12). Note that there is typically some cancellation of errors between the exchange ($E_x$) and correlation ($E_c$) contributions to $E_{xc}$. The “energy barrier” is the barrier to a chemical reaction that arises at a highly-bonded intermediate state.

<table>
<thead>
<tr>
<th>Property</th>
<th>LSD</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x$</td>
<td>5% (not negative enough)</td>
<td>0.5%</td>
</tr>
<tr>
<td>$E_c$</td>
<td>100% (too negative)</td>
<td>5%</td>
</tr>
<tr>
<td>bond length</td>
<td>1% (too short)</td>
<td>1% (too long)</td>
</tr>
<tr>
<td>structure</td>
<td>overly favors close packing</td>
<td>more correct</td>
</tr>
<tr>
<td>energy barrier</td>
<td>100% (too low)</td>
<td>30% (too low)</td>
</tr>
</tbody>
</table>

Table 1.2. Mean absolute error of the atomization energies for 20 molecules, evaluated by various approximations. (1 hartree = 27.21 eV) (From [20])

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Mean absolute error (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unrestricted Hartree-Fock</td>
<td>3.1 (underbinding)</td>
</tr>
<tr>
<td>LSD</td>
<td>1.3 (overbinding)</td>
</tr>
<tr>
<td>GGA</td>
<td>0.3 (mostly overbinding)</td>
</tr>
<tr>
<td>Desired “chemical accuracy”</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 1.3. Exchange-correlation energies of atoms, in hartree

<table>
<thead>
<tr>
<th>Atom</th>
<th>LSD</th>
<th>GGA</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>−0.29</td>
<td>−0.31</td>
<td>−0.31</td>
</tr>
<tr>
<td>He</td>
<td>−1.00</td>
<td>−1.06</td>
<td>−1.09</td>
</tr>
<tr>
<td>Li</td>
<td>−1.69</td>
<td>−1.81</td>
<td>−1.83</td>
</tr>
<tr>
<td>Be</td>
<td>−2.54</td>
<td>−2.72</td>
<td>−2.76</td>
</tr>
<tr>
<td>N</td>
<td>−6.32</td>
<td>−6.73</td>
<td>−6.78</td>
</tr>
<tr>
<td>Ne</td>
<td>−11.78</td>
<td>−12.42</td>
<td>−12.50</td>
</tr>
</tbody>
</table>

Table 1.4. Atomization energies of molecules, in eV. (1 hartree = 27.21 eV).
From [20]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>LSD</th>
<th>GGA</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>4.9</td>
<td>4.6</td>
<td>4.7</td>
</tr>
<tr>
<td>CH₄</td>
<td>20.0</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>NH₃</td>
<td>14.6</td>
<td>13.1</td>
<td>12.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>11.6</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>CO</td>
<td>13.0</td>
<td>11.7</td>
<td>11.2</td>
</tr>
<tr>
<td>O₂</td>
<td>7.6</td>
<td>6.2</td>
<td>5.2</td>
</tr>
</tbody>
</table>
The Lyon interactions: how were they constrained?

- a good reproduction of the saturation point of the symmetric infinite nuclear matter, i.e. $\rho_0 \simeq 0.16 \text{ fm}^{-3}$, $E/A \simeq -16 \text{ MeV}$,
- a compression modulus of the symmetric nuclear matter $K_\infty \simeq 230 \text{ MeV}$,
- a symmetry energy $a_S \simeq 32 \text{ MeV}$,
- an enhancement factor of the Thomas–Reiche–Kuhn sum rule $\kappa = 0.25$ (energy weighted sum rule occurring in the E1; $T = 1$ giant dipole resonance),
- a reasonable reproduction of the Wiringa et al. [8] equation of state for pure neutron matter,
- a good reproduction (see Table 5 in part I) of the binding energies of doubly magic nuclei – $^{16}\text{O}$, $^{40,48}\text{Ca}$, $^{56}\text{Ni}$, $^{132}\text{Sn}$ and $^{208}\text{Pb}$ – as well as their r.m.s. radii when experimentally known,
- no constraint on the surface properties.

Large importance of nuclear matter and of neutron matter (as the electron gas for usual DFT)
Consensus on the need of a larger set of data (UNEDF)

Spherical Nuclei

• Masses, r.m.s. radii, diffraction radii and surface thickness
• Giant monopole and dipole resonance in $^{90}$Zr, $^{116}$Sn and $^{208}$Pb
• Experimental energy of the first 2+ state and B(E2) value in Ca, Ni, Sn and Pb isotopes

Axially-deformed Nuclei

• Binding energy of well-deformed even-even nuclei.
• Super-deformed bandheads and fission isomers

Symmetry-unrestricted

• Ground-state spin and parity for odd-mass nuclei (odd-even, even-odd and odd-odd)
• High-K terminating states in f-p shell nuclei
• 1q.p. excited states of odd-mass heaviest elements
All correlations in the interaction?

- There should be according to the DFT!
- BUT: form of the functional is unknown
- Double counting problem if correlations are added to a density functional

- It is better to avoid in the density functional correlations which vary rapidly with A
- Physical interpretations could be more obvious if beyond mean-field correlations are explicitly treated (rotational and vibrational correlations)
- Spectra, transition probabilities?
Example: shell effects far from stability

- How do shell effects evolve with N and Z far from stability?
- Quenching of shell effects?
- Coupling between the continuum and the bound sp states?

- M. Bender, G. Bertsch, P.-H. Heenen:
  Calculation of the ground state of all e-e nuclei including correlations due to symmetry restorations and configuration mixing
Shell effects far from stability

- New magic numbers far from stability
- Shell quenching due to the coupling to the continuum
- Change of the form of the mean-field?
- Tensor force?
- Why not correlations beyond mean field?

Bender, Bertsch and Heenen systematic calculations of ground state energies of e-e nuclei

Mean-field + symmetry restorations + configuration mixing