ELECTRONIC STRUCTURE: BASICS AND DFT

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THE PROBLEM:
NUCLEI AND ELECTRONS INTERACTING VIA COULOMB FORCES

- Hamiltonian of the universe

\[ H = T_n + V_{nn} + T_e + V_{ee} + V_{ne} \]

\[ T_n = -\frac{\hbar^2}{2} \sum_{i=1}^{P} \frac{1}{M_i} \nabla_i^2 \]

\[ V_{nn} = \frac{e^2}{2} \sum_{i=1}^{P} \sum_{j=1}^{P} \frac{Z_i Z_j}{|R_i - R_j|} \]

\[ T_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \]

\[ V_{ee} = \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \frac{1}{|r_i - r_j|} \]

\[ V_{ne} = -\frac{e^2}{2} \sum_{i=1}^{N} \sum_{I=1}^{P} \frac{Z_I}{|r_i - R_I|} \]

- Schrödinger equation:

\[ i\hbar \frac{\partial \Psi(r, R; t)}{\partial t} = H\Psi(r, R; t) \]

\[ r = \{r_i\} \quad i = 1, \ldots, N \]

\[ R = \{R_I\} \quad I = 1, \ldots, P \]
ADIABATIC APPROXIMATION

- Adiabatic expansion:
  \[ \Psi(r, R; t) = \sum_{\alpha} \Theta_{\alpha}(R; t) \Phi_{\alpha}(r; R) \]

- Electronic Hamiltonian:
  \[ h_e(R) = T_e + V_{ee} + V_{ne}(R) = H - T_n - V_{nn} \]

- Electronic Schrödinger equation:
  \[ \hbar \Phi_{\alpha}(r; R) = E_{\alpha}(R) \Phi_{\alpha}(r; R) \]

- Replacing into TD-Schrödinger:
  \[ \left\{ i\hbar \frac{\partial}{\partial t} + T_n + V_{nn} - E_{\alpha}(R) \right\} \Theta_{\alpha}(R; t) = \sum_{l=1}^{P} \frac{\hbar^2}{2M_l} \left\langle \Phi_{\alpha} \left| \nabla_l^2 \right| \Phi_{\alpha} \right\rangle \Theta_{\alpha}(R; t) + \]
  \[ 2 \sum_{\beta} \sum_{l=1}^{P} \frac{\hbar^2}{2M_l} \left[ \nabla_l \Theta_{\beta}(R; t) \right] \cdot \left\langle \Phi_{\alpha} \left| \nabla_l \right| \Phi_{\beta} \right\rangle \]

\[ d_{\alpha\beta} = \text{Non-adiabatic couplings} \]

Describe non-radiative transitions originated in the nuclear motion
ADIABATIC APPROXIMATION

- Condition for adiabaticity:

\[
\frac{m}{M_I} \left| \frac{\hbar \Omega_v}{E_\alpha(R) - E_\beta(R)} \right| << 1
\]

- \( \Omega_v \) = frequency of rotation of the electronic wave function due to nuclear motion

- For \( \frac{m}{M} \sim 5 \times 10^{-4} \) (proton), vibrational energies (\( \hbar \Omega_v \sim 0.01 \text{ eV} \)) are two orders of magnitude smaller than electronic excitation energies (\( \Delta E \sim 1 \text{ eV} \)) \( \Rightarrow \)

\textbf{Adiabatic electronic eigenstates do not mix}

\[
\Psi(r,R;t) = \Theta_\alpha(R;t) \Phi_\alpha(r;R)
\]

\( \alpha \) does not change in time, e.g. \( \alpha = 0 \) (Ground State)

- Adiabatic Schrödinger equation:

\[
\left\{ i\hbar \frac{\partial}{\partial t} + T_\text{n} + V_\text{nn} - E_\alpha(R) - \sum_{l=1}^{P} \frac{\hbar^2}{2M_l} \left\langle \Phi_\alpha \left| \nabla_{l}^2 \right| \Phi_\alpha \right\rangle \right\} \Theta_\alpha(R;t) = 0
\]
ADIABATIC APPROXIMATION

- Time scale associated to the motion of the nuclei much slower than that of electrons → *Electrons follow instantaneously the nuclear motion, without changing electronic eigenstate.*

- **Non-adiabaticity**: along the dynamical evolution, two (or more) electronic levels can get very close, so that $\Delta E \approx \hbar \Omega_v$, and the adiabatic approximation breaks down.

- *This can also happen because nuclear motion is very fast, e.g. swift ions.*
CLASSICAL NUCLEI APPROXIMATION

- At room T: $\lambda_T \approx 0.1 \text{ Å}$
- No phase coherence beyond

Nuclear wave function can be approximated as a Hartree product:

$$\Theta_\alpha (\mathbf{R}; t) = \prod I \theta_\alpha (\mathbf{R}_I, \mathbf{R}_I^{(c)}; t)$$

XC energy density of the HEG

- Nuclei are generally quite well localized. The larger the mass, the better localized they are $\Rightarrow$

  **Nuclei can be considered classical particles**

- **Ehrenfest theorem:**

  $$i\hbar \frac{d\langle \mathbf{R}_I \rangle}{dt} = \langle [H, \mathbf{R}_I] \rangle = \frac{i\hbar}{M_I} \langle \mathbf{P}_I \rangle \Rightarrow M_I \frac{d\langle \mathbf{R}_I \rangle}{dt} = \langle \mathbf{P}_I \rangle$$

  $$i\hbar \frac{d\langle \mathbf{P}_I \rangle}{dt} = \langle [H, \mathbf{P}_I] \rangle = -i\hbar \langle \nabla_I E_\alpha (\mathbf{R}) \rangle$$
CLASSICAL NUCLEI APPROXIMATION

- Leads to Newton-like equations:

\[
M_I \frac{d^2 \langle R_I \rangle}{dt^2} = -\langle \nabla_I E_\alpha (R) \rangle
\]

1. Nuclear wave function approximated as a product of \( \delta \)-functions, centred at the classical position: \( R_I^{(c)}(t) \)

\[
\Theta_\alpha (R; t) \approx \prod_I \delta (R_I - R_I^{(c)}(t))
\]

2. Expectation value of the force approximated as the gradient of the potential energy surface (PES) at the classical position

\[
\langle \nabla_I E_\alpha (R) \rangle \approx \nabla_I E_\alpha (R_I^{(c)}) = \frac{\partial E_\alpha (R_I^{(c)})}{\partial R_I^{(c)}}
\]

*Strictly valid only for \( \delta \)-functions or harmonic potentials*

- In some situations, e.g. spontaneous phonon emission, electronic transitions require quantum nuclei (A. Fisher)
SUMMARY

- This leads to:
  \[ M_I \frac{d^2 \mathbf{R}_I^{(c)}}{dt^2} = -\nabla I E_\alpha (\mathbf{R}_I^{(c)}) \]
  \[ \nabla I E_\alpha (\mathbf{R}_I^{(c)}) = 0 \]

- and:

- Both, geometry optimization and first-principles MD require the solution of the time-independent Schrödinger equation for a system of \( N \) interacting electrons in the external Coulomb field of the nuclei

- \[ h_e \Phi_\alpha (\mathbf{r}; \mathbf{R}^{(c)}) = E_\alpha (\mathbf{R}^{(c)}) \Phi_\alpha (\mathbf{r}; \mathbf{R}^{(c)}) \]

Electronic structure
A quantum many-body problem
PHYSICAL ORIGIN OF MANY-BODY EFFECTS: CORRELATION

- Electrochemical cell: charge in the electrodes depends on the potential difference (Gouy-Chapman, 1901-1913)

- Two concepts
  1. Screening length
  2. Plasma frequency

- Many-body: electrons interact with each other

- Electrostatic potential generated by electrons verifies Poisson’s equation:

\[ \nabla^2 V_H(r) = 4\pi e \left\{ -e \delta(r) - en(r) + e\bar{n} \right\} \]

- Pair correlation function:

\[ g(r) = n(r) / \bar{n} \]
PHYSICAL ORIGIN OF MANY-BODY EFFECTS: CORRELATION

- Poisson’s equation:

\[ \nabla^2 V_H (\mathbf{r}) = -4\pi e^2 \left\{ \delta(\mathbf{r}) + \bar{n}[g(\mathbf{r}) - 1] \right\} \]

The presence of an electron discourages the other electrons from approaching it: CORRELATION

- \( g(r) \) is the probability of finding two electrons at a distance \( r \).
PHYSICAL ORIGIN OF MANY-BODY EFFECTS: CORRELATION

- **Classical liquid (Boltzmann):**
  \[ g(r) = \exp\left(-\frac{V_H(r)}{k_B T}\right) \]

- Linearizing:
  \[ g(r) \approx 1 - \frac{V_H(r)}{k_B T} \]

- Replacing \( g(r) \) into Poisson’s equation \( \Rightarrow \) linearized Poisson-Boltzmann:
  \[ \nabla^2 V_H(r) = -4\pi e^2 \delta(r) + \frac{1}{l_{DH}^2} V_H(r) \]

- **Screened Coulomb** interaction:
  \[ V_H(r) = \frac{e^2}{r} \exp\left(-\frac{r}{l_{DH}}\right) \]

- **Debye-Hückel** screening length:
  \[ l_{DH} = \sqrt{\frac{k_B T}{4\pi \bar{n} e^2}} \]
PHYSICAL ORIGIN OF QUANTUM MANY-BODY EFFECTS: SCREENING

- **Quantum (electron) liquid:**

  Electric field interacts with $q$

  $$E_q(r) = q\left\{ \sum_{l=1}^{P} \frac{Z_le}{|r - R_l|} + \int \frac{(-e)n(r')}{|r - r'|} \, dr' \right\}$$

- If $q$ is just one electron amongst the others, then it is not a test charge anymore, and **will displace some charge $\delta n(r)$ [static screening charge] to make space for itself.**

- Electron-electron interaction:

  $$V_{ee}(r) = -\sum_{l=1}^{P} \frac{Z_le^2}{|r - R_l|} + e^2\int \frac{[n(r') + \delta n(r')]\, dr'}{|r - r'|}$$
Replacing into Schrödinger equation:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 - \sum_{I=1}^{P} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + e^2 \int \frac{n_r(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + e^2 \int \frac{\delta n_r(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \varphi_n(\mathbf{r}; \mathbf{R}) = \varepsilon_n(\mathbf{R}) \varphi_n(\mathbf{r}; \mathbf{R})
\]

**Pauli principle:**

\[
n(\mathbf{r}; \mathbf{R}) = \sum_{n=1}^{N} |\varphi_n(\mathbf{r}; \mathbf{R})|^2 \quad \text{(self-consistency)}
\]

1. **Fermi-Dirac statistics** ⇒ Exchange (statistical correlation)
2. **Non-statistical correlations**
   1. **Static**: electrons spatially separated (multi-configuration, left-right)
   2. **Dynamic**: fluctuations in electronic density (Van der Waals)
THE HOMOGENEOUS ELECTRON GAS (HEG) (JELLILUM)

- Random Phase Approximation (RPA):
  \[
  \delta n(\mathbf{r}) = -\frac{mk_F^2}{2\pi^3\hbar^2} \int V_H(\mathbf{r}') \frac{j_1(2k_F |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
  \]

- Dielectric function (in reciprocal space):
  \[
  V_H(\mathbf{k}) = \frac{4\pi e^2}{k^2} \frac{1}{\varepsilon(\mathbf{k})}
  \]

- In the RPA (Lindhard):
  \[
  \varepsilon(k) = 1 + \frac{2mk_F e^2}{\pi\hbar^2 k^2} \left\{ 1 + \frac{k_F}{k} \left( \frac{k^2}{k_F^2} - 1 \right) \ln \left| \frac{k - 2k_F}{k + 2k_F} \right| \right\}
  \]

1. **Thomas-Fermi** (small k)
   \[
   V_H(k) \sim \frac{4\pi e^2}{k^2 + k_{TF}^2}
   \]

2. **k→2k_F**: Friedel oscillations at long distance
   \[
   V_H(r) \sim \frac{e^2}{r} \exp(-k_{TF} r)
   \]
WAVFUNCTION APPROACHES IN QUANTUM CHEMISTRY

- Many-electron problem:
  \[ h_e \Phi_\alpha (\mathbf{r}; \mathbf{R}) = E_\alpha (\mathbf{R}) \Phi_\alpha (\mathbf{r}; \mathbf{R}) \]

- Hartree product (uncorrelated):
  \[ \Phi_\alpha (\mathbf{r}; \mathbf{R}) = \prod_{n=1}^{N} \varphi_n (\mathbf{r}_n ; \mathbf{R}) \]

- Replacing into Schrödinger’s equation:
  \[
  \left[ -\frac{\hbar^2}{2m} \nabla^2 + V^{(n)}_{\text{eff}} (\mathbf{r}; \mathbf{R}) \right] \varphi_n (\mathbf{r}; \mathbf{R}) = \varepsilon_n (\mathbf{R}) \varphi_n (\mathbf{r}; \mathbf{R})
  \]
  \[ V^{(n)}_{\text{eff}} (\mathbf{r}; \mathbf{R}) = V_{\text{ext}} (\mathbf{r}; \mathbf{R}) + \int \frac{\sum_{j \neq n} \rho_j (\mathbf{r}'; \mathbf{R})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \]

- Electronic density
  \[ \rho_j (\mathbf{r}; \mathbf{R}) = |\varphi_j (\mathbf{r}; \mathbf{R})|^2 \]

- Total density
  \[ \rho (\mathbf{r}; \mathbf{R}) = \sum_{j=1}^{N} \rho_j (\mathbf{r}; \mathbf{R}) \]

Self-interaction removed

Electronic density
WAVEFUNCTION APPROACHES: HARTREE-FOCK

- Hartree-Fock (Exchange only): Slater determinant

\[
\Phi_\alpha (\mathbf{r}, \mathbf{R}) = SD\{\varphi_n (\mathbf{r}_j)\} = \frac{1}{\sqrt{N!}} \begin{pmatrix}
\varphi_1 (\mathbf{r}_1) & \varphi_1 (\mathbf{r}_2) & \cdots & \varphi_1 (\mathbf{r}_N) \\
\varphi_2 (\mathbf{r}_1) & \varphi_2 (\mathbf{r}_2) & \cdots & \varphi_2 (\mathbf{r}_N) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_N (\mathbf{r}_1) & \varphi_N (\mathbf{r}_2) & \cdots & \varphi_N (\mathbf{r}_N)
\end{pmatrix}
\]

- Hartree-Fock equations: Self-interaction free, no correlation

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext} (\mathbf{r}; \mathbf{R}) + \sum_{j=1}^{N} \int \frac{\rho_j (\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} - \sum_{j=1}^{N} \int \frac{\varphi_j^* (\mathbf{r'}; \mathbf{R}) \varphi_n (\mathbf{r'}; \mathbf{R})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} \right] \varphi_n (\mathbf{r}; \mathbf{R}) = \sum_{j=1}^{N} \lambda_{nj} (\mathbf{R}) \varphi_j (\mathbf{r}; \mathbf{R})
\]

- Direct Coulomb

- Exchange

- \[ \sum_{j=1}^{N} \lambda_{nj} (\mathbf{R}) \varphi_j (\mathbf{r}; \mathbf{R}) \]
WAVEFUNCTION APPROACHES: HARTREE-FOCK AND BEYOND

- Total energy:

\[ E_{\alpha}^{\text{Hartree}}(\mathbf{R}) = \sum_{n=1}^{N} \varepsilon_n(\mathbf{R}) - \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} J_{jk} \]

\[ E_{\alpha}^{\text{HF}}(\mathbf{R}) = \sum_{n=1}^{N} \varepsilon_n(\mathbf{R}) - \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} (J_{jk} - K_{jk}) \]

\[ J_{jk} = \iint \frac{\rho_j(\mathbf{r})\rho_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' \]

\[ K_{jk} = \iint \frac{\phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r}')\phi_k(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' \]

- To introduce Static and Dynamical Correlation:
  1. Møller-Plesset perturbation theory on HF wave function: MP\textsubscript{2}, MP\textsubscript{4}, Coupled-clusters (re-summation to \(\infty\) order): CCSD(T)
  2. Configuration interaction (CI): CISD(T)
  3. Multi-reference methods: CASSCF, CASMP\textsubscript{2}, MR-CI
ELECTRON-ELECTRON INTERACTION: GENERAL

- Electron-electron interaction:
  \[
  E_{ee} = \frac{1}{2} \iiint \frac{\rho(r)\rho(r')}{|r-r'|} \, drdr' + \frac{1}{2} \iiint \frac{\rho(r)\rho(r')}{|r-r'|} \left[g(r,r') - 1\right] \, drdr'
  \]
  \textbf{Direct Coulomb (Hartree) \quad Pair correlation function}

- Total energy:
  \[
  E = T_e + V_{ext} + E_{ee} = T_e + V_{ext} + \frac{1}{2} \iiint \frac{\rho(r)\rho(r')}{|r-r'|} \, drdr' + E_x + E_C
  \]
  \textbf{Exchange \quad Correlation}

- External:
  \[
  E_{ext} = \sum_{l=1}^{P} \rho(r)V_{ext}^{(l)}(r - R_l) \, dr
  \]

- Kinetic:
  \[
  T_e = -\frac{\hbar^2}{2m} \left\langle \Phi(R) \sum_{n=1}^{N} \nabla_n^2 \Phi(R) \right\rangle = -\frac{\hbar^2}{2m} \int \left[\nabla_r^2 \rho_1(r,r')\right]_{r'=r} \, dr
  \]
DENSITY FUNCTIONAL THEORY (DFT): THE ANCESTORS

- Thomas-Fermi (1927): Approximation for the kinetic energy from the homogeneous electron gas.

\[ T_{TF} = \int t_{TF}[\rho] \rho(r) \, dr = \int \left[ \frac{3}{5} \frac{\hbar^2}{2m} (3\pi)^{2/3} \rho^{2/3} \right] \rho(r) \, dr = C_K \int \rho^{5/3}(r) \, dr \]

\[ E_{TF}[\rho] = C_K \int \rho^{5/3}(r) \, dr + \int V_{ext}(r) \rho(r) \, dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr' \]

- Minimizing the functional with respect to \( \rho(r) \), under the constraint that \( \rho(r) \) integrates to \( N \), we obtain an integral equation for \( \rho(r) \):

\[ \frac{5}{3} C_K \rho^{2/3}(r) + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} \, dr' = \mu \]

\[ E_X[\rho] = -C_X \int \rho^{4/3}(r) \, dr \]

\[ E_C[\rho] = -\int A \rho^{4/3} / (B + \rho^{1/3}) \, dr \]

\[ T_{WW}[\rho] = \frac{1}{8} \int (|\nabla \rho|^2 / \rho) \, dr \]

\( \mu = \text{electronic chemical potential} \)

Dirac exchange
Wigner correlation
Von Weizsäcker gradient correction
DENSITY FUNCTIONAL THEORY (DFT): MODERN THEORY

- **Hohenberg-Kohn theorem** (1964): Two external local potentials differing only in an additive constant, correspond to the same electronic density
  \[ \rho(r) \Leftrightarrow V_{\text{ext}}(r), N \]

- **V-representability** (Levy 1982): Not any density is allowed. It must arise from some external potential ⇒ constrained search

- **Minimum principle**: \( E_v[\rho] = T_e + V_{\text{ext}}[\rho] + E_{ee}[\rho] \) is minimum for \( \rho_{\text{GS}} = \text{ground state density} \).

- **Variational equations**: \( \delta [E_v[\rho] - \mu \left( \int \rho(r) dr \right)] = 0 \)
  \[ \frac{\delta E_v[\rho]}{\delta \rho(r)} = V_{\text{ext}}(r) + \frac{\delta F[\rho]}{\delta \rho(r)} = \mu \]
  \( F[\rho] = T_e[\rho] + E_{ee}[\rho] \)
  A universal functional (depends only on the interaction)
HK theorem is valid for any e-e interaction $U$, including the full Coulomb interaction, and also $U=0$, corresponding to non-interacting electrons.

**Non-interacting reference system** $(R)$: a system of non-interacting electrons, i.e. $U_R=0$, with the same density $\rho$ of the system of interacting electrons ($U=V_{ee}$).

\[
\rho_R(r) = \sum_{n=1}^{N} |\varphi^R_n(r)|^2 = \rho(r)
\]

The reference orbitals correspond to non-interacting electrons. Therefore, they are solutions of the Schrödinger equation in an effective, reference “external” potential $V_R[\rho](r)$:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_R[\rho](r) \right] \varphi^R_n(r) = \varepsilon_n \varphi^R_n(r)
\]
DENSITY FUNCTIONAL THEORY (DFT): NON-INTERACTING REFERENCE SYSTEM

- The reference orbitals $\varphi_n^R(\mathbf{r})$ are implicit functionals of the electronic density.

- **Energy of non-interacting electrons:**

$$E_R[\rho] = T_R[\rho] + \int V_R(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- **Non-interacting kinetic energy known explicitly:**

$$T_R[\rho] = \sum_{n=1}^{N} \int \varphi_n^{* R}(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_n^R(\mathbf{r}) d\mathbf{r}$$

- Any functional of the reference orbitals is, implicitly, a functional of the electronic density via the mapping:

$$\rho(\mathbf{r}) \leftrightarrow V_R[\rho] \leftrightarrow \left\{ \varphi_n^R(\mathbf{r}) \right\} \leftrightarrow T_R[\rho]$$
DENSITY FUNCTIONAL THEORY (DFT): EXCHANGE-CORRELATION

- For the interacting system, define the Exchange-Correlation functional as:

\[
E_{XC}[\rho] = F[\rho] - \frac{1}{2} \iiint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' - T_R[\rho]
\]

- Which is different \((T_R[\rho] \neq T[\rho])\) from

\[
E_{XC}^{\text{int}}[\rho] = F[\rho] - \frac{1}{2} \iiint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' - T[\rho]
\]

- The HK variational energy functional is, then:

\[
E_v[\rho] = T_R[\rho] + \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \iiint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho]
\]

- Thomas-Fermi methods approximate also \(T_R[\rho]\) **Only unknown term**

\textit{Fast, but not very accurate}
DENSITY FUNCTIONAL THEORY (DFT): KOHN-SHAM METHODS

- **Kohn-Sham** (1965): Use exact kinetic functional for reference orbitals and approximate \( E_{XC}[\rho] \)

Minimizing \( E_v[\rho] \) with respect to \( \rho \):

\[
0 = \frac{\delta E_v[\rho]}{\delta \rho(r)} = \frac{\delta T_R[\rho]}{\delta \rho(r)} + V_{\text{ext}}(r) + V_H(r) + \mu_{XC}[\rho](r)
\]

\( V_{KS}[\rho](r) = \text{Kohn-Sham potential} \)

- With the exchange-correlation potential defined as:

\[
\mu_{XC}[\rho](r) = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)}
\]

- Using the relation (always valid):

\[
\frac{\delta T_R[\rho]}{\delta \rho(r)} = -V_R[\rho](r)
\]

We find that the reference potential coincides with the Kohn-Sham potential

\[
V_R[\rho](r) = V_{KS}[\rho](r) = V_{\text{ext}}(r) + V_H(r) + \mu_{XC}[\rho](r)
\]
DENSITY FUNCTIONAL THEORY (DFT):
KOHN-SHAM EQUATIONS

- **Kohn-Sham equations:**

\[
\begin{bmatrix}
-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[\rho](\mathbf{r})
\end{bmatrix}
\psi_n^{KS} (\mathbf{r}) = \varepsilon_n \psi_n^{KS} (\mathbf{r})
\]

\[
\rho_{KS}(\mathbf{r}) = \rho(\mathbf{r}) = \sum_{n=1}^{N} |\psi_n^{KS}(\mathbf{r})|^2
\]

where **interacting** and **Kohn-Sham** electronic densities are enforced to be equal

- This leads to a partial differential equation that has to be solved self-consistently, as the KS potential depends on the density, which is constructed with the solutions of the KS equations.
DENSITY FUNCTIONAL THEORY (DFT):
KOHN-SHAM EQUATIONS

- **Observations regarding Kohn-Sham equations:**
  1. The true interacting many-body wave function **is not a Slater determinant** of the KS orbitals.
  2. The electronic density constructed with the KS orbitals is, by construction, the same as that from the true wave function.
  3. $E_{XC}[\rho]$ must contain **kinetic correlations** absent in $T_R[\rho]$.
  4. The non-interacting reference systems does not necessarily exist with integer occupations of the KS orbitals. This is cured by extending the domain of definition of occupation numbers $\{f_n\}$ to any real number between 0 and 1.
  5. **Janak’s theorem** ($I=-\mu=-\varepsilon_{\text{max}}$) is valid.
  6. **Koopman’s theorem** ($\Delta E=E(N+1)-E(N)\neq \varepsilon_{N+1}-\varepsilon_N$) is not valid, but Slater’s $\Delta$SCF method works out very nicely.
How to obtain $E_{XC}$ that includes kinetic correlations?

Start from the non-interacting systems and switch gradually the Coulomb interaction, always maintaining the same density.

$$H_\lambda = T + V_{ext} + \lambda V_{ee}$$

**Adiabatic connection**

$$E_{XC}[\rho] = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} \left[ \tilde{g}(r,r') - 1 \right] dr dr'$$

$$\tilde{g}(r,r') = \int_0^1 g_\lambda(r,r') d\lambda$$

**Langreth-Perdew 1977**

In practice, $E_{XC}$ is obtained as the difference: $E_{XC}[\rho] = E_{XC}[\rho] + T[\rho] - T_K[\rho]$

**Exchange**: no $\lambda$-average

* Taken from “exact” QMC calculations

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**DENSITY FUNCTIONAL THEORY (DFT): ADIABATIC CONNECTION**
DENSITY FUNCTIONAL THEORY (DFT): EXCHANGE-CORRELATION HOLE

- Coupling constant averaged pair correlation function:
  \[ \tilde{g}_{XC}(\mathbf{r}, \mathbf{r}') = g_x(\mathbf{r}, \mathbf{r}') + \tilde{g}_c(\mathbf{r}, \mathbf{r}') \]

- Exchange-correlation hole:
  \[ E_{XC}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\tilde{\rho}_{XC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' \]
  \[ \tilde{\rho}_{XC}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}')[g_x(\mathbf{r}, \mathbf{r}')] + \rho(\mathbf{r}')[\tilde{g}_c(\mathbf{r}, \mathbf{r}') - 1] \]

- Sum rules:
  - Exchange hole contains one missing electron
  - Correlation hole integrates to 0

- Symmetry: \( \tilde{g}(\mathbf{r}, \mathbf{r}') = \tilde{g}(\mathbf{r}', \mathbf{r}) \)

- Normalization

- Should cancel self-interaction

- Hartree

- Exact

- HF
The inhomogeneous electron gas is considered as locally homogeneous:

\[
E_{XC}[\rho] = \int \rho(r) \varepsilon_{XC}^{LDA}[\rho](r) \, dr
\]

\[
\varepsilon_{XC}^{LDA}[\rho] = \int \tilde{\rho}_{XC}^{LDA}(r,r') \, dr'
\]

**XC energy density of the HEG**

\[
\tilde{g}_{XC}^{LDA}(r,r') = \tilde{g}_{XC}^{HEG}(|r-r'|, \rho(r)) \left[ \frac{\rho(r)}{\rho(r')} \right]
\]

- LDA XC hole centred at \( r \), interacts with the electron also at \( r \).
  The exact XC hole is centred at \( r' \)
- This is partially compensated by multiplying the pair correlation function with the density ratio \( \rho(r)/\rho(r') \)
EXCHANGE AND CORRELATION IN DFT: THE LOCAL DENSITY APPROXIMATION (LDA)

Location of the XC hole (Jones and Gunnarsson, 1982)
LDA-LSDA: TRENDS AND LIMITATIONS

- Favors more homogeneous electron densities
- Overbinds molecules and solids (Hartree-Fock underbinds)
- Geometries, bond lengths and angles, vibrational frequencies reproduced within 2-3%
- Dielectric constants overestimated by about 10%
- Bond lengths too short for weakly bound systems (H-bonds, VDW)
- Correct chemical trends, e.g. ionization energies
- Atoms (core electrons) poorly described (HF is much better)
- XC potential decays exponentially into vacuum regions. It should decay as $-e^2/r$. Hence, it is poor for dissociation and ionization
- Poor for metallic surfaces and physisorption
- Very poor for negatively charged ions (self-interaction error)
- Poor for weakly bound systems: H-bonds ($\nabla \rho$), VDW (non-local)
- Band gap in semiconductors too small (~40%)
- Poor for strong on-site correlations ($d$ and $f$ systems, oxides, UO$_2$)
BEYOND THE LDA

- Inhomogeneities in the density
- Self-interaction cancellation
- Non-locality in exchange and correlation
- Strong local correlations

- Gradient expansions
- Weighted density approximation
- Exact exchange in DFT (OEP local vs HF non-local)
- DFT-HF hybrids
- Self-interaction correction
- Van der Waals and RPA functionals
- LSDA+U
- Multi-reference Kohn-Sham
- GW approximation (Many-body)
GRADIENT EXPANSIONS:
GENERALIZED GRADIENT APPROXIMATION

- $E_{XC}$ expanded in gradients of the density

$$E_{GGA}[\rho] = \int \rho(r) \varepsilon_{XC}^{LSDA}[\rho, \zeta](r) F_{XC}[\rho, \zeta, s](r) dr$$

where $\zeta$ is the spin polarization
$s = |\nabla \rho|/2k_F\rho$ is the density gradient
And $F_{XC}$ is the enhancement factor

- First-order term is fine, but higher-order terms diverge. Only by some re-summation to $\infty$-order the expansion converges.

- **GGA:** $F_{XC}$ is designed to fulfil a number of exactly known properties, e.g. Perdew-Burke-Ernzerhof (PBE)
  1. **Exchange:** uniform scaling, LSDA limit, spin-scaling relationship, LSDA linear response, Lieb-Oxford bound
  2. **Correlation:** second-order expansion, hole sum rule, vanishes for rapidly varying densities, cancels singularity at high densities
Properties of the GGA

- Improves atomization and surface energies
- Favors density inhomogeneities
- Increases lattice parameters of metals
- Favors non-spherical distortions
- Improves bond lengths
- Improves energies and geometries of H-bonded systems
- There is error cancellation between X and C at short range

- XC potential still decays exponentially into vacuum regions
- Some improvement in band gaps in semiconductors
- What was correct in LDA is worsened in GGA
- Still incorrect dissociation limit. Fractionally charged fragments
- Inter-configurational errors in $I_p$ and $E_A$
- Error cancellation between X and C is not complete at long-range. X hole is more long-ranged than XC hole
HYBRID FUNCTIONALS

- Combine GGA local exchange with Hartree-Fock non-local exchange:

\[ E_{HYBRID}[\rho] = \alpha E_{X}^{GGA}[\rho] + (1 - \alpha) E_{X}^{HF}[\rho] + E_{C}^{GGA}[\rho] \]

- Parameter \( \alpha \) fitted to experimental data for molecules (~0.75), or determined from known properties.

- PBE0, B3LYP, HSE06

- **Properties:**
  1. Quite accurate in many respects, e.g. energies and geometries
  2. Improve on the self-interaction error, but not fully SI-free
  3. Improve on band gaps
  4. Improve on electron affinities
  5. Better quality than MP2
  6. Fitted hybrids unsatisfactory from the theoretical point of view
SELF-INTERACTION CORRECTION (SIC)

- Self-interaction can be removed at the level of classical electrostatics:
  \[
  E_H = \frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} d\mathbf{r} d\mathbf{r}'
  \]

\[E_{SIC} = E_H - \frac{1}{2} \sum_{n=1}^{N} \iint \frac{\rho_n(r) \rho_n(r')}{|r - r'|} d\mathbf{r} d\mathbf{r}'\]

\[V_{SIC}^{(n)}(\mathbf{r}) = V_H(\mathbf{r}) - \int \frac{\rho_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\]

- Potential is state-dependent. Hence it is not an eigenvalue problem anymore, but a system of coupled PDEs

- Orthogonality of SIC orbitals not guaranteed, but it can be imposed (Suraud)

- Similar to HF, but the Slater determinant of SIC orbitals is not invariant against orbital transformations

- The result depends on the choice of orbitals (localization)
Van der Waals (dispersion) interactions: are a dynamical non-local correlation effect

Dipole-induced dipole interaction due to quantum density fluctuations in spatially separated fragments

Functional (Dion et al 2004):

\[ E_{VDW} = \int \int \rho(r) \phi(r, r') \rho(r') \, dr \, dr' \]

\( \phi = \text{VDW kernel fully non-local.} \)
\( \text{Depends on } \rho(r) \text{ and } \rho(r') \)

Expensive double integral

Efficient implementations (Roman-Perez and Soler 2009)

Good approximations based on dynamical response theory

Beyond VDW: Random Phase Approximation (Furche)
LSDA+U

- Strong onsite Coulomb correlations are not captured by LDA/GGA
- These are important for localized \((d\) and \(f\)) electronic bands, where many electrons share the same spatial region: **self-interaction problem**

- Semi-empirical solution: separate occupied and empty state by an additional energy \(U\) as in Hubbard’s model:
  \[
  E_{LSDA+U} = E_{LSDA} - \frac{1}{2} U N(N-1) + \frac{1}{2} U \sum_{i \neq j} f_i f_j
  \]
  \(f_i = \) orbital occupations

- This induces a splitting in the KS eigenvalues:
  \[
  \begin{align*}
  \mathcal{E}_i &= \frac{\partial E_{LSDA+U}}{\partial f_i} = \mathcal{E}_{LSDA} + U \left( \frac{1}{2} - f_i \right) \\
  \mathcal{E}_{i \text{occ}} &= \mathcal{E}_{i \text{LSDA}} - U/2 \\
  \mathcal{E}_{i \text{empty}} &= \mathcal{E}_{i \text{LSDA}} + U/2
  \end{align*}
  \]
SUMMARY OF DFT APPROXIMATIONS