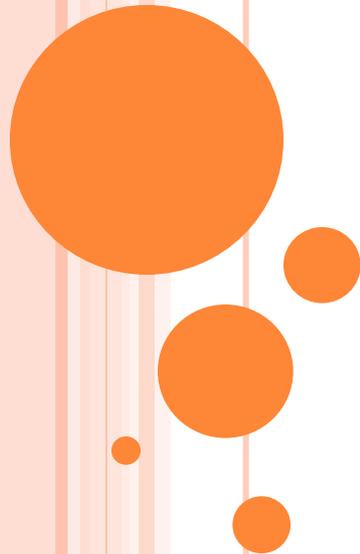


ELECTRONIC STRUCTURE: BASICS AND DFT

**Jorge Kohanoff
Queen's University Belfast
United Kingdom**

j.kohanoff@qub.ac.uk



THE PROBLEM:

NUCLEI AND ELECTRONS INTERACTING VIA COULOMB FORCES

○ Hamiltonian of the universe

$$H = T_n + V_{nn} + T_e + V_{ee} + V_{ne}$$

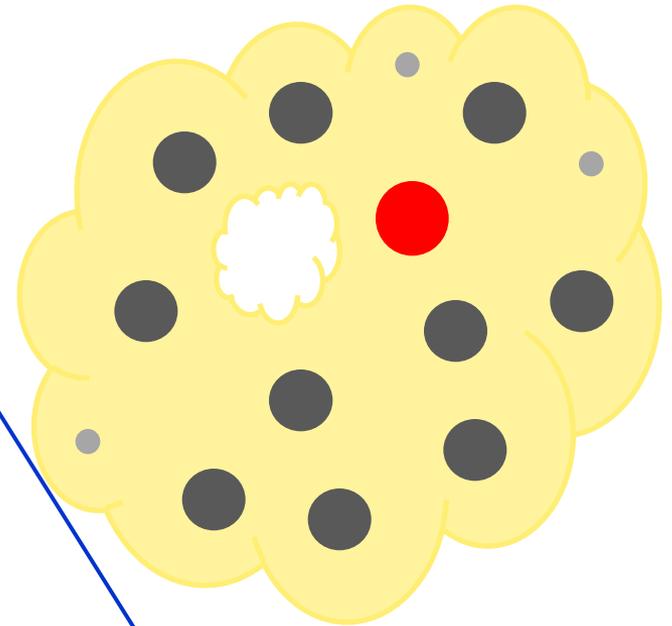
$$T_n = -\frac{\hbar^2}{2} \sum_{I=1}^P \frac{1}{M_I} \nabla_I^2$$

$$V_{nn} = \frac{e^2}{2} \sum_{I=1}^P \sum_{J \neq I}^P \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

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

$$V_{ee} = \frac{e^2}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_{ne} = -\frac{e^2}{2} \sum_{i=1}^N \sum_{I=1}^P \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$



○ Schrödinger equation:

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

$$\mathbf{r} = \{\mathbf{r}_i\} \quad i=1, \dots, N$$

$$\mathbf{R} = \{\mathbf{R}_I\} \quad I=1, \dots, P$$



ADIABATIC APPROXIMATION

- Adiabatic expansion:

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_{\alpha} \Theta_{\alpha}(\mathbf{R}; t) \Phi_{\alpha}(\mathbf{r}; \mathbf{R})$$

- Electronic Hamiltonian:

$$h_e(\mathbf{R}) = T_e + V_{ee} + V_{ne}(\mathbf{R}) = H - T_n - V_{nn}$$

- Electronic Schrödinger equation:

$$h_e \Phi_{\alpha}(\mathbf{r}; \mathbf{R}) = E_{\alpha}(\mathbf{R}) \Phi_{\alpha}(\mathbf{r}; \mathbf{R})$$

- Replacing into TD-Schrödinger:

$$\left\{ i\hbar \frac{\partial}{\partial t} + T_n + V_{nn} - E_{\alpha}(\mathbf{R}) \right\} \Theta_{\alpha}(\mathbf{R}; t) = \sum_{I=1}^P \frac{\hbar^2}{2M_I} \langle \Phi_{\alpha} | \nabla_I^2 | \Phi_{\alpha} \rangle \Theta_{\alpha}(\mathbf{R}; t) + 2 \sum_{\beta} \sum_{I=1}^P \frac{\hbar^2}{2M_I} [\nabla_I \Theta_{\beta}(\mathbf{R}; t)] \cdot \underbrace{\langle \Phi_{\alpha} | \nabla_I | \Phi_{\beta} \rangle}_{d_{\alpha\beta}}$$

$d_{\alpha\beta}$ = Non-adiabatic couplings

Describe non-radiative transitions originated in the nuclear motion

ADIABATIC APPROXIMATION

- Condition for adiabaticity:

$$\frac{m}{M_I} \left| \frac{\hbar \Omega_v}{E_\alpha(\mathbf{R}) - E_\beta(\mathbf{R})} \right| \ll 1$$

- Ω_v = frequency of rotation of the electronic wave function due to nuclear motion
- For $m/M \sim 5 \times 10^{-4}$ (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

Adiabatic electronic eigenstates do not mix

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \Theta_\alpha(\mathbf{R}; t) \Phi_\alpha(\mathbf{r}; \mathbf{R})$$

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

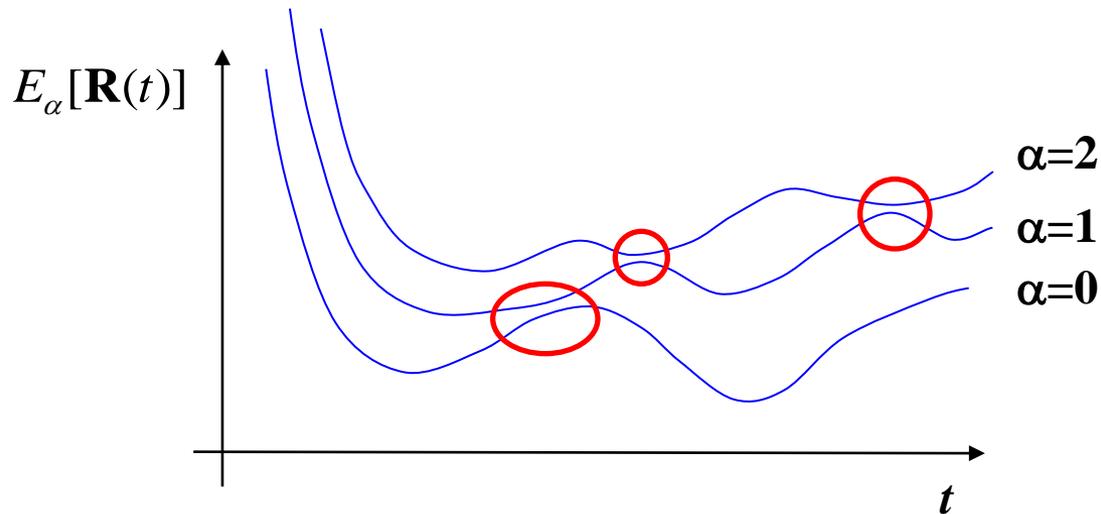
- Adiabatic Schrödinger equation:

$$\left\{ i\hbar \frac{\partial}{\partial t} + T_n + V_{nn} - E_\alpha(\mathbf{R}) - \sum_{I=1}^P \frac{\hbar^2}{2M_I} \langle \Phi_\alpha | \nabla_I^2 | \Phi_\alpha \rangle \right\} \Theta_\alpha(\mathbf{R}; t) = 0$$



ADIABATIC APPROXIMATION

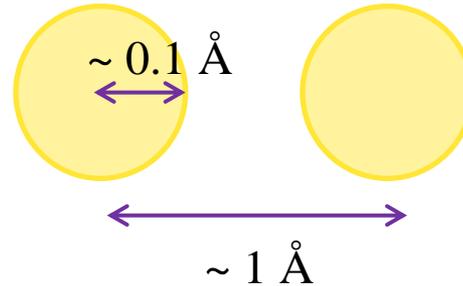
- Time scale associated to the motion of the nuclei much slower than that of electrons → *Electrons follow instantaneously the nuclear motion, without changing electronic eigenstate.*
- *Non-adiabaticity*: along the dynamical evolution, two (or more) electronic levels can get very close, so that $\Delta E \approx \hbar\Omega_v$, 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: $\lambda_T \approx 0.1 \text{ \AA}$
- No phase coherence beyond

- Nuclear wave function can be approximated as a Hartree product:

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

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:

$$M_I \frac{d^2 \langle \mathbf{R}_I \rangle}{dt^2} = -\langle \nabla_I E_\alpha(\mathbf{R}) \rangle$$

1. Nuclear wave function approximated as a product of δ -functions, centred at the classical position: $\mathbf{R}_I^{(c)}(t)$

$$\Theta_\alpha(\mathbf{R}; t) \approx \prod_I \delta(\mathbf{R}_I - \mathbf{R}_I^{(c)}(t))$$

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

$$\langle \nabla_I E_\alpha(\mathbf{R}) \rangle \approx \nabla_I E_\alpha(\mathbf{R}_I^{(c)}) = \frac{\partial E_\alpha(\mathbf{R}_I^{(c)})}{\partial \mathbf{R}_I^{(c)}}$$

Strictly valid only for δ -functions or harmonic potentials

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



SUMMARY

- This leads to:

$$M_I \frac{d^2 \mathbf{R}_I^{(c)}}{dt^2} = -\nabla_I E_\alpha(\mathbf{R}_I^{(c)})$$

*First-principles (quantum)
Molecular Dynamics*

- and:

$$\nabla_I E_\alpha(\mathbf{R}_I^{(c)}) = 0$$

Geometry optimization

- 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*

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

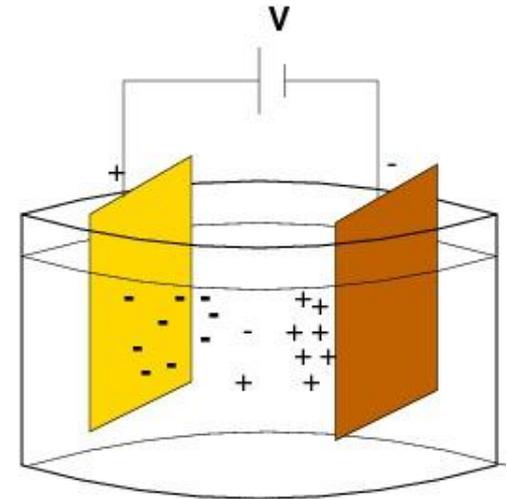
Electronic structure

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:



$$\nabla^2 V_H(\mathbf{r}) = 4\pi e \{ -e\delta(\mathbf{r}) - en(\mathbf{r}) + e\bar{n} \}$$

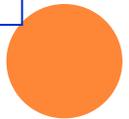
e^- at origin

other e^-

neutralizing background

- Pair correlation function:

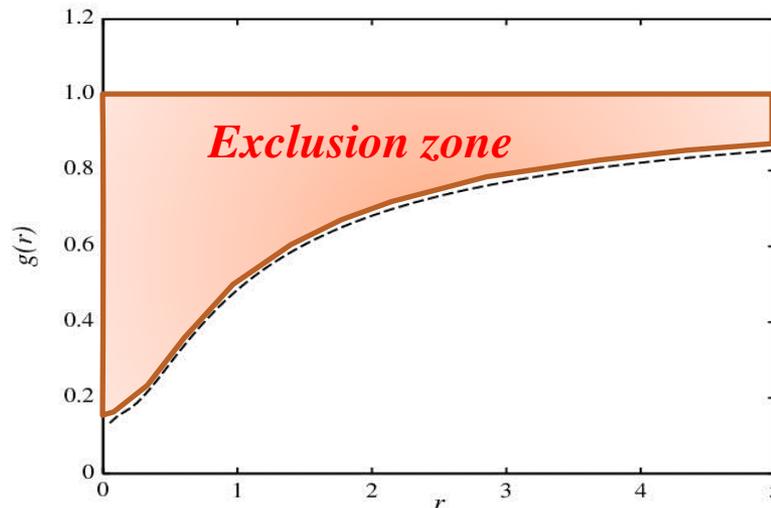
$$g(\mathbf{r}) = n(\mathbf{r}) / \bar{n}$$



PHYSICAL ORIGIN OF MANY-BODY EFFECTS: CORRELATION

- Poisson's equation:

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



*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):

$$g(r) = \exp(-V_H(r)/k_B T)$$

- Linearizing:

$$g(r) \approx 1 - V_H(r)/k_B T$$

- Replacing $g(r)$ into Poisson's equation \Rightarrow linearized Poisson-Boltzmann:

$$\nabla^2 V_H(\mathbf{r}) = -4\pi e^2 \delta(\mathbf{r}) + \frac{1}{l_{DH}^2} V_H(\mathbf{r})$$

- **Screened Coulomb** interaction:

$$V_H(\mathbf{r}) = \frac{e^2}{r} \exp(-r/l_{DH})$$

- **Debye-Hückel** screening length:

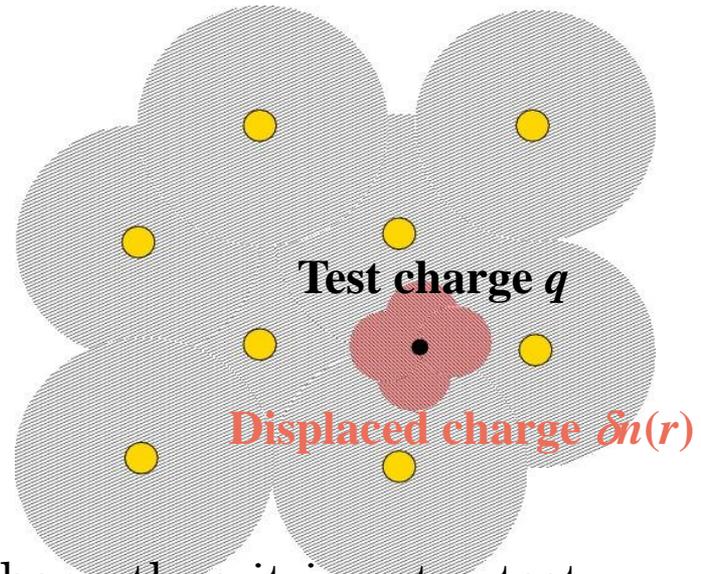
$$l_{DH} = \sqrt{\frac{k_B T}{4\pi \bar{n} e^2}}$$



PHYSICAL ORIGIN OF QUANTUM MANY-BODY EFFECTS: SCREENING

- Quantum (electron) liquid:
- Electric field interacts with q

$$\mathbf{E}_q(\mathbf{r}) = q \left\{ \sum_{I=1}^P \frac{Z_I e}{|\mathbf{r} - \mathbf{R}_I|} + \int \frac{(-e)n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right\}$$



- 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:

$$V_{ee}(\mathbf{r}) = - \sum_{I=1}^P \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + e^2 \int \frac{[n(\mathbf{r}') + \delta n(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$



PHYSICAL ORIGIN OF QUANTUM MANY-BODY EFFECTS: SCREENING

- Replacing into Schrödinger equation:

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

V_{en}
Nuclei
 V_H
Classical electrostatics
 V_{Screen}
Correlation

- Pauli principle:

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

1. Fermi-Dirac statistics \Rightarrow 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) (JELLIUM)

- 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):

$$V_H(\mathbf{k}) = \frac{4\pi e^2}{k^2} \frac{1}{\epsilon(\mathbf{k})}$$

- In the RPA (Lindhard):

$$\epsilon(k) = 1 + \frac{2mk_F e^2}{\pi\hbar^2 k^2} \left\{ 1 + \frac{k_F}{k} \left(\frac{k^2}{k_F^2} - 1 \right) \ln \left| \frac{k - 2k_F}{k + 2k_F} \right| \right\}$$

1. **Thomas-Fermi** (small k)

$$V_H(k) \sim \frac{4\pi e^2}{k^2 + k_{TF}^2}$$

$$\longrightarrow V_H(r) \sim \frac{e^2}{r} \exp(-k_{TF} r)$$

2. $k \rightarrow 2k_F$: **Friedel oscillations at long distance**

WAVEFUNCTION APPROACHES IN QUANTUM CHEMISTRY

- Many-electron problem:

$$\hat{h}_e \Phi_\alpha(\mathbf{r}; \mathbf{R}) = E_\alpha(\mathbf{R}) \Phi_\alpha(\mathbf{r}; \mathbf{R})$$

- 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:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}^{(n)}(\mathbf{r}; \mathbf{R}) \right] \varphi_n(\mathbf{r}; \mathbf{R}) = \varepsilon_n(\mathbf{R}) \varphi_n(\mathbf{r}; \mathbf{R})$$

$$V_{\text{eff}}^{(n)}(\mathbf{r}; \mathbf{R}) = V_{\text{ext}}(\mathbf{r}; \mathbf{R}) + \int \frac{\sum_{j \neq n}^N \rho_j(\mathbf{r}'; \mathbf{R})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

*Self-
interaction
removed*

$$\rho_j(\mathbf{r}; \mathbf{R}) = |\varphi_j(\mathbf{r}; \mathbf{R})|^2$$

$$\rho(\mathbf{r}; \mathbf{R}) = \sum_{j=1}^N \rho_j(\mathbf{r}; \mathbf{R})$$

*Electronic
density*



WAVEFUNCTION APPROACHES: HARTREE-FOCK

- Hartree-Fock (*Exchange only*): Slater determinant

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

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

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

WAVEFUNCTION APPROACHES: HARTREE-FOCK AND BEYOND

- Total energy:

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

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

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

Coulomb integrals

$$K_{jk} = \iint \frac{\varphi_j^*(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_k(\mathbf{r})\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

Exchange integrals

- To introduce *Static and Dynamical Correlation*:
 - Møller-Plesset perturbation theory on HF wave function: **MP2**, **MP4**, Coupled-clusters (re-summation to ∞ order): **CCSD(T)**
 - Configuration interaction (CI): **CISD(T)**

$$\Phi_{\alpha}(\mathbf{r}, \mathbf{R}) = \sum_{i_1, \dots, i_N} c_{i_1, \dots, i_N} SD\{\varphi_{i_1}(\mathbf{r}_1) \cdots \varphi_{i_N}(\mathbf{r}_N)\}$$
 - Multi-reference methods: **CASSCF**, **CASMP2**, **MR-CI**

ELECTRON-ELECTRON INTERACTION: GENERAL

- Electron-electron interaction:

$$E_{ee} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [g(\mathbf{r},\mathbf{r}')-1] d\mathbf{r}d\mathbf{r}'$$

Direct Coulomb (Hartree)

Pair correlation function

- Total energy:

$$E = T_e + V_{ext} + E_{ee} = T_e + V_{ext} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_X + E_C$$

Exchange Correlation

- External:

$$E_{ext} = \sum_{I=1}^P \rho(\mathbf{r}) V_{ext}^{(I)}(\mathbf{r} - \mathbf{R}_I) d\mathbf{r}$$

- Kinetic:

$$T_e = -\frac{\hbar^2}{2m} \left\langle \Phi(\mathbf{R}) \left| \sum_{n=1}^N \nabla_n^2 \right| \Phi(\mathbf{R}) \right\rangle = -\frac{\hbar^2}{2m} \int [\nabla_{\mathbf{r}}^2 \rho_1(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r}$$



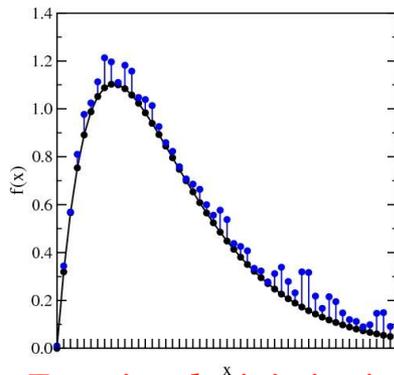
DENSITY FUNCTIONAL THEORY (DFT): THE ANCESTORS

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

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

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

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



Functional minimization

$$\frac{5}{3} C_K \rho^{2/3}(\mathbf{r}) + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \mu$$

*$\mu = \text{electronic}$
 $\text{chemical potential}$*

$$E_X[\rho] = -C_X \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

Dirac exchange

$$E_C[\rho] = -\int A \rho^{4/3} / (B + \rho^{1/3}) d\mathbf{r}$$

Wigner correlation

$$T_{vw}[\rho] = \frac{1}{8} \int (|\nabla \rho|^2 / \rho) d\mathbf{r}$$

*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**

$$\rho(\mathbf{r}) \Leftrightarrow V_{ext}(\mathbf{r}), N$$

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

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

- Variational equations: $\delta \left[E_v[\rho] - \mu \left(\int \rho(\mathbf{r}) d\mathbf{r} \right) \right] = 0$

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = V_{ext}(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} = \mu$$

$$F[\rho] = T_e[\rho] + E_{ee}[\rho]$$

*A universal functional
(depends only on the interaction)*



DENSITY FUNCTIONAL THEORY (DFT): NON-INTERACTING REFERENCE SYSTEM

- 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 ρ of the system of interacting electrons ($U=V_{ee}$)**.

$$\rho_R(\mathbf{r}) = \sum_{n=1}^N |\varphi_n^R(\mathbf{r})|^2 = \rho(\mathbf{r})$$

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

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_R[\rho](\mathbf{r}) \right] \varphi_n^R(\mathbf{r}) = \varepsilon_n \varphi_n^R(\mathbf{r})$$



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:

$$\rho(\mathbf{r}) \Leftrightarrow V_R[\rho] \Leftrightarrow \{\varphi_n^R(\mathbf{r})\} \Leftrightarrow T_R[\rho]$$



DENSITY FUNCTIONAL THEORY (DFT): EXCHANGE-CORRELATION

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

$$E_{xc}[\rho] = F[\rho] - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - T_R[\rho]$$

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

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

- The HK variational energy functional is, then:

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

- Thomas-Fermi methods approximate also $T_R[\rho]$

Only unknown term

Fast, but not very accurate

DENSITY FUNCTIONAL THEORY (DFT): KOHNSHAM METHODS

- **Kohn-Sham** (1965): Use exact kinetic functional for reference orbitals and approximate $E_{XC}[\rho]$
- Minimizing $E_v[\rho]$ with respect to ρ :

$$0 = \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_R[\rho]}{\delta \rho(\mathbf{r})} + \underbrace{V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \mu_{XC}[\rho](\mathbf{r})}_{V_{KS}[\rho](\mathbf{r})}$$

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

- With the exchange-correlation potential defined as:

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

- Using the relation (always valid):

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

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

$$V_R[\rho](\mathbf{r}) = V_{KS}[\rho](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \mu_{XC}[\rho](\mathbf{r})$$



DENSITY FUNCTIONAL THEORY (DFT): KOHNSHAM EQUATIONS

- Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[\rho](\mathbf{r}) \right] \varphi_n^{KS}(\mathbf{r}) = \varepsilon_n \varphi_n^{KS}(\mathbf{r})$$
$$\rho_{KS}(\mathbf{r}) = \rho(\mathbf{r}) = \sum_{n=1}^N |\varphi_n^{KS}(\mathbf{r})|^2$$

- 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): KOHNSHAM 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** ($I = -\mu = -\varepsilon_{max}$) 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 Δ SCF method works out very nicely.

$$\rho(\mathbf{r}) = \sum_{n=1}^N f_n |\varphi_n^{KS}(\mathbf{r})|^2$$

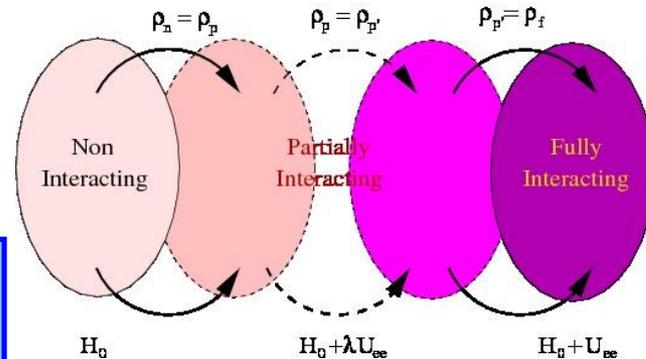


DENSITY FUNCTIONAL THEORY (DFT): ADIABATIC CONNECTION

- 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



$$E_{XC}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [\tilde{g}(\mathbf{r},\mathbf{r}') - 1] d\mathbf{r}d\mathbf{r}'$$

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

Langreth-Perdew 1977

- In practice, E_{XC} is obtained as the difference: $E_{XC}[\rho] = \underbrace{E_{XC}[\rho] + T[\rho]}_{\text{exact}} - T_R[\rho]$
- Exchange:** no λ -average

Taken from "exact" QMC calculations

DENSITY FUNCTIONAL THEORY (DFT): EXCHANGE-CORRELATION HOLE

- Coupling constant averaged pair correlation function:

$$\tilde{g}_{XC}(\mathbf{r}, \mathbf{r}') = g_X(\mathbf{r}, \mathbf{r}') + \tilde{g}_C(\mathbf{r}, \mathbf{r}')$$

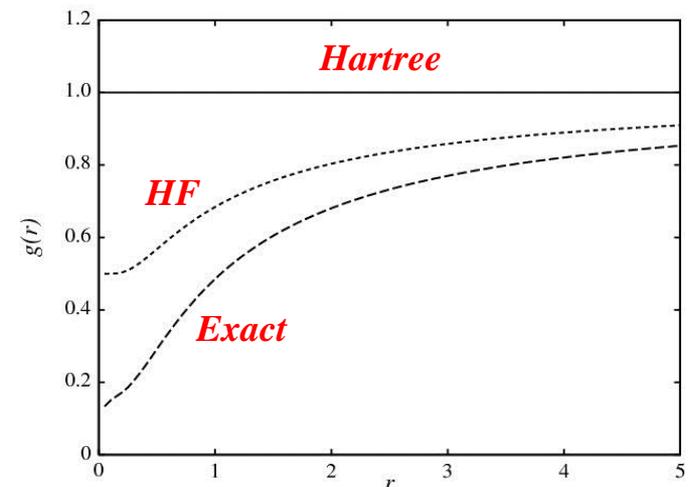
- Exchange-correlation hole:

$$E_{XC}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \tilde{\rho}_{XC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$\tilde{\rho}_{XC}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') [g_X(\mathbf{r}, \mathbf{r}')] + \rho(\mathbf{r}') [\tilde{g}_C(\mathbf{r}, \mathbf{r}') - 1]$$

- 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



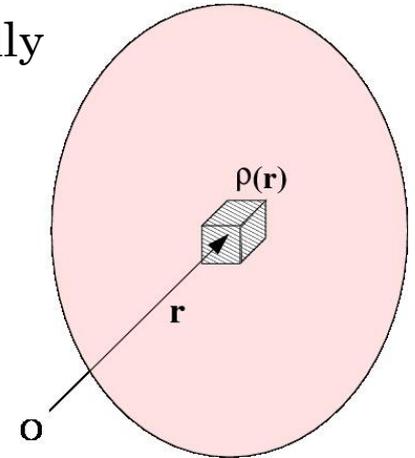
EXCHANGE AND CORRELATION IN DFT: THE LOCAL DENSITY APPROXIMATION (LDA)

- The inhomogeneous electron gas is considered as locally homogeneous:

$$E_{XC}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{XC}^{LDA}[\rho](\mathbf{r}) d\mathbf{r}$$

$$\varepsilon_{XC}^{LDA}[\rho] = \int \frac{\tilde{\rho}_{XC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

XC energy density of the HEG



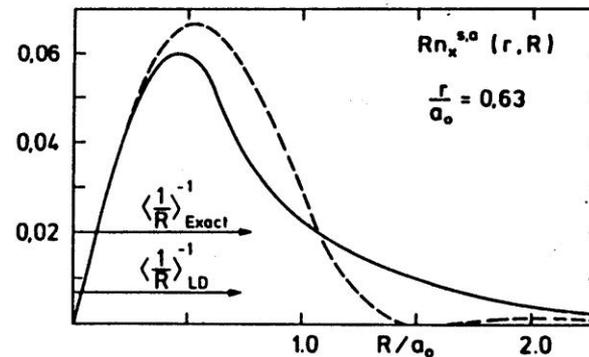
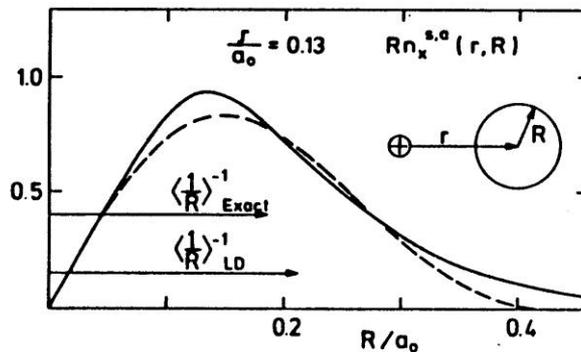
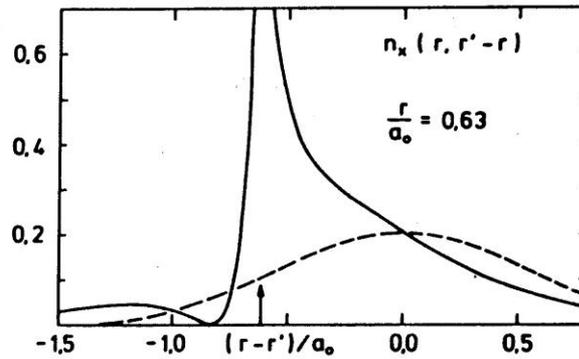
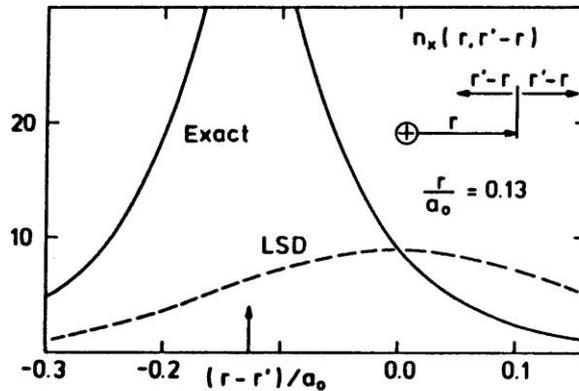
$$\tilde{g}_{XC}^{LDA}(\mathbf{r}, \mathbf{r}') = \tilde{g}_{XC}^{HEG}(|\mathbf{r} - \mathbf{r}'|, \rho(\mathbf{r})) \left[\frac{\rho(\mathbf{r})}{\rho(\mathbf{r}')} \right]$$

- LDA XC hole centred at \mathbf{r}** , interacts with the electron also at \mathbf{r} .
The exact XC hole is centred at \mathbf{r}'
- This is partially compensated by multiplying the pair correlation function with the density ratio $\rho(\mathbf{r})/\rho(\mathbf{r}')$



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 ($\sim 40\%$)
- 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

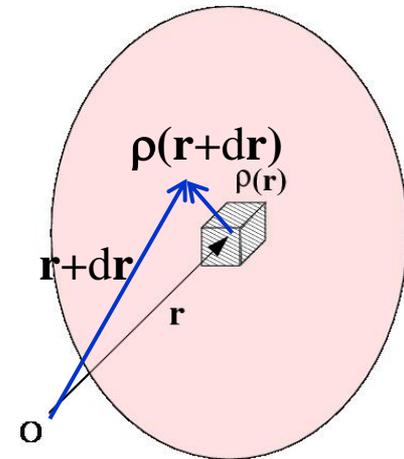
- E_{XC} expanded in gradients of the density

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

where ζ 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 ∞ -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 α 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:

$$E_H = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

Perdew-Zunger 1982
Mauri, Sprik, Suraud

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

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

- 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)**



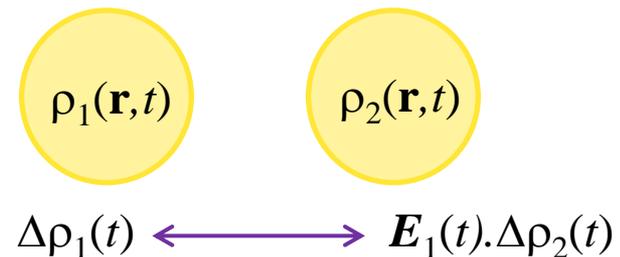
VAN DER WAALS FUNCTIONALS

- 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):*

$$E_{\text{VDW}} = \iint \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

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



- **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:

$$\varepsilon_i = \frac{\partial E_{LSDA+U}}{\partial f_i} = \varepsilon_i^{LSDA} + U \left(\frac{1}{2} - f \right)$$

$$\begin{aligned} \varepsilon_i^{occ} &= \varepsilon_i^{LSDA} - U/2 \\ \varepsilon_i^{empty} &= \varepsilon_i^{LSDA} + U/2 \end{aligned}$$



SUMMARY OF DFT APPROXIMATIONS

