DFT, RDMFT, and the challenge of strong correlations

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האוניברסיטה העברית בירושלים THE HEBREW UNIVERSITY OF JERUSALEM الجامعة العبرية في اورشليم القدس

Electronic-Structure Problem:

Hamiltonian of N electrons moving in the field of clamped nuclei (Born-Oppenheimer approximation):

$$\left(\hat{\mathrm{T}}_{e}(\underline{\underline{r}}) + \hat{\mathrm{V}}_{ee}(\underline{\underline{r}}) + \hat{\mathrm{V}}_{en}(\underline{\underline{r}},\underline{\underline{R}}) \right) \Phi_{\underline{\underline{R}}}^{\mathrm{BO}}(\underline{\underline{r}}) = \in^{\mathrm{BO}}(\underline{\underline{R}}) \Phi_{\underline{\underline{R}}}^{\mathrm{BO}}(\underline{\underline{r}})$$

for fixed nuclear configuration $\underline{\mathbf{R}}$.

This is an exponentially hard problem!!

Why don't we just solve the many-particle SE?

Example: Aluminium atom (13 electrons)

 $\Psi(\vec{r}_1,...,\vec{r}_{13})$ depends on 39 coordinates

rough table of the wavefunction

10 entries per coordinate: $\Rightarrow 10^{39}$ entries1 byte per entry: $\Rightarrow 10^{39}$ bytes 10^{12} bytes per SSD: $\Rightarrow 10^{27}$ SSDs20 g per SSD: $\Rightarrow 2 \times 10^{28}$ g SSDs

For Ti atom the required mass of SSDs exceeds mass of the universe **Two fundamentally different classes of ab-initio approaches:**

- Wave function approaches
 - -- Quantum Monte Carlo
 - -- Configuration interaction
 - -- Tensor product decomposition/DMRG

Scaling of algorithms often less than exponential!

• "Functional Theories"

Two fundamentally different classes of ab-initio approaches:

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"<u>Functional Theories</u>"

Write total energy as functional of a simpler quantity and minimize

MBPT RDMFT DFT $G(r, r', t - t') \quad \gamma(r, r') = G(r, r', 0^+) \quad \rho(r) = \gamma(r, r)$

MBPTRDMFTDFTG(r,r',t-t') $\gamma(r,r') = G(r,r',0^+)$ $\rho(r) = \gamma(r,r)$ <u>Functional:</u><u>Functional:</u><u>Functional:</u> $\Phi_{xc}[G]$ $E_{xc}[\gamma]$ $E_{xc}[\rho]$ or $\Sigma_{xc}[G]$ or $v_{xc}[\rho]$

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OUTLINE

- Basics of Density-Functional Theory (DFT)
- Magnetism and superconductivity within DFT
- Basics of Reduced-Density-Matrix-Functional Theory (RDMFT)
- Approximate functionals
- **RDMFT** results for molecules
- Towards RDMFT for strongly correlated solids

ESSENCE OF DENSITY-FUNTIONAL THEORY

- Every observable quantity of a quantum system can be calculated from the density of the system ALONE
- The density of particles interacting with each other can be calculated as the density of an auxiliary system of <u>non-interacting particles</u>

ESSENCE OF DENSITY-FUNTIONAL THEORY

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Hohenberg-Kohn theorem (1964) Kohn-Sham theorem (1965) (for the ground state)



HOHENBERG-KOHN THEOREM

1.
$$v(r) \leftarrow 1 \longrightarrow \rho(r)$$

one-to-one correspondence between external potentials v(r) and ground-state densities $\rho(r)$. Consequence: Many-body WF is uniquely determined by the density, $\Psi = \Psi[\rho]$, and hence all expectation values w.r.t. $\Psi[\rho]$ are functionals of $\rho(r)$.

2. <u>Variational principle</u>

Given a particular system characterized by the external potential $v_0(r)$. There exists a functional, $E_{HK}[\rho]$, such that the solution of the Euler-Lagrange equation

$$\frac{\delta}{\delta\rho(\mathbf{r})} \mathbf{E}_{\mathrm{HK}}[\rho] = 0$$

yields the exact ground-state energy E_0 and ground-state density $\rho_0(\mathbf{r})$ of this system

3.
$$E_{HK}[\rho] = \langle \Psi[\rho] | T + V_{ee} + V_0 | \Psi[\rho] \rangle = F[\rho] + \int \rho(r) v_0(r) d^3r$$

F[ρ] is <u>UNIVERSAL</u>. **In practice**, **F**[ρ] needs to be approximated

KOHN-SHAM EQUATIONS

Rewrite HK functional as:

$$E_{HK}[\rho] = T_{S}[\rho] + \int \rho(r) v_{0}(r) d^{3}r + E_{H}[\rho] + E_{xc}[\rho]$$

where $T_{S}[\rho]$ is the kinetic energy functional of non-interacting particles

$$\frac{\delta}{\delta \rho(\mathbf{r})} \mathbf{E}_{\mathrm{HK}}[\rho] = 0$$
 yields the Kohn-Sham equations:

$$\left(-\nabla^{2} / 2 + v_{o}(\mathbf{r}) + v_{H}[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})\right)\phi_{j}(\mathbf{r}) = \in_{j} \phi_{j}(\mathbf{r})$$

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<u>Walter Kohn</u>: "The KS equations are an exactification of the Hartree mean-field equation". It yields the true density of the interacting system.

 $E_{xc}[\rho]$ is a universal functional of the density which, in practice, needs to be approximated (e.g. LDA, GGAs, metaGGAs, hybrid functionals).

The functional $E_{xc}[\rho]$ is <u>universal</u>:

Curse or blessing?





DFT description of quantum phases: Magnetism and Superconductivity **MAGNETIC SYSTEMS**

Quantity of interest: Spin magnetization density m(r)

In principle, Hohenberg-Kohn theorem guarantees that m(r) is a functional of the density: $m(r) = m[\rho](r)$. In practice, good approximations for the functional $m[\rho]$ are not known.

Include m(r) as basic variable in the formalism, in addition to the density $\rho(r)$.

MAGNETIC SYSTEMS

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Start from fully interacting Hamiltonian with Zeeman term:

$$\hat{H}_{v,\vec{B}} = \hat{T} + \hat{V}_{ee} + \int \hat{\rho}(r) v(r) d^3 r - \int \hat{\vec{m}}(r) \cdot \vec{B}(r) d^3 r$$
$$\hat{\vec{m}}(r) = \mu_0 \sum_{\alpha\beta} \hat{\psi}^+_{\alpha}(r) \vec{\sigma}_{\alpha\beta} \hat{\psi}_{\beta}(r)$$

HK theorem

$$\left[\rho(r), \vec{m}(r)\right] \xleftarrow{1-1} \left[v(r), \vec{B}(r)\right]$$

total energy:

$$E_{v,\vec{B}}[\rho,\vec{m}] = F[\rho,\vec{m}] + \int d^{3}r \left(v(r)\rho(r) - \vec{B}(r) \cdot \vec{m}(r)\right)$$

universal



For simplicity:
$$\vec{B}(r) = \begin{pmatrix} 0 \\ 0 \\ B(r) \end{pmatrix}$$
, $\vec{m}(r) = \begin{pmatrix} 0 \\ 0 \\ m(r) \end{pmatrix}$

$$\left(-\frac{\nabla^2}{2m} + \left[\mathbf{v}(\mathbf{r}) + \mathbf{v}_{\mathrm{H}}(\mathbf{r}) + \mathbf{v}_{\mathbf{xc}}(\mathbf{r})\right] \pm \mu_{\mathrm{o}}\left[\mathbf{B}(\mathbf{r}) - \mathbf{B}_{\mathbf{xc}}(\mathbf{r})\right]\right) \Phi_{\pm}^{j}(\mathbf{r}) = \epsilon_{\pm}^{j} \Phi_{\pm}^{j}(\mathbf{r})$$

 $v_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta \rho$ $B_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta m$

 $\rho(\mathbf{r}) = \rho_{+}(\mathbf{r}) + \rho_{-}(\mathbf{r}) , m(\mathbf{r}) = \rho_{+}(\mathbf{r}) - \rho_{-}(\mathbf{r}) , \rho_{\pm} = \Sigma |\varphi_{\pm}^{j}|^{2}$

$\underline{B \longrightarrow 0}$ limit

These equations do <u>not</u> reduce to the original KS equations for $B \rightarrow 0$ if, in this limit, the system has a finite m(r).

DENSITY-FUNTIONAL THEORY OF THE SUPERCONDUCTING STATE

BASIC IDEA:

• Include order parameter, χ , characterising superconductivity as additional "density"

L.N. Oliveira, E.K.U.G., W. Kohn, PRL 60, 2430 (1988)

General (model-independent) characterization of superconductors: Off-diagonal long-range order of the 2-body density matrix:

$$\rho^{(2)}(\mathbf{x}\mathbf{x'},\mathbf{y}\mathbf{y'}) = \left\langle \hat{\psi}_{\downarrow}^{+}(\mathbf{x'})\hat{\psi}_{\uparrow}^{+}(\mathbf{x})\hat{\psi}_{\uparrow}(\mathbf{y})\hat{\psi}_{\downarrow}(\mathbf{y'})\right\rangle$$



$$\chi$$
 (r,r') = $\langle \hat{\psi}_{\uparrow}(r) \hat{\psi}_{\downarrow}(r') \rangle$

order parameter of the N-S phase transition

ANALOGY



"proximity effect"

Hamiltonian

$$\hat{H}_{e} = \hat{T}_{e} + \hat{W}_{ee} + \int \hat{\rho}(\mathbf{r}) v(\mathbf{r}) d^{3}r - \int d^{3}r \int d^{3}r' \left(\hat{\chi}(\mathbf{r},\mathbf{r'}) \Delta^{*}(\mathbf{r},\mathbf{r'}) + \text{H.c.} \right)$$

 $\mathbf{E}_{\mathbf{x}\mathbf{c}} = \mathbf{E}_{\mathbf{x}\mathbf{c}}[\boldsymbol{\rho},\boldsymbol{\chi}]$

Basics of Reduced Density Matrix Functional Theory

One-body reduced density matrix (1-RDM)

• for integer particle number N:

 $\gamma_{\mathrm{N}}(\vec{r},\vec{r}') = \mathbf{N} \times \int L \int \Psi_{\mathrm{N}}^{*}(\vec{r}',\vec{x}_{2},\ldots\vec{x}_{\mathrm{N}}) \Psi_{\mathrm{N}}(\vec{r},\vec{x}_{2},\ldots\vec{x}_{\mathrm{N}}) d^{3}x_{2}\ldots d^{3}x_{\mathrm{N}}$

• for fractional particle number $M = N_0 + \omega$ ($0 \le \omega \le 1$) $\gamma(\vec{r}, \vec{r}') = (1 - \omega) \gamma_{N_0}(\vec{r}, \vec{r}') + \omega \gamma_{N_0+1}(\vec{r}, \vec{r}')$

Diagonalization yields the natural orbitals $\phi_j(\vec{r})$ and their occupation numbers n_i :

$$\int \gamma (\vec{r}, \vec{r}') \phi_j(\vec{r}') d^3r' = n_j \phi_j(\vec{r})$$

Central Theorem by Gilbert (1975): There is a rigorous 1-1 correspondence $\Psi_{gs}(r_1, r_2, ..., r_N) \longleftrightarrow \gamma(\mathbf{r}, \mathbf{r'})$

- Total energy is a unique functional $E[\gamma]$ of the 1-RDM
- Ground-state energy can be calculated by minimizing $E[\gamma]$ $E_{tot}[\gamma] = E_{kin}[\gamma] + \int v_{ext}(\vec{r})\gamma(\vec{r},\vec{r})d^{3}r + E_{H}[\gamma] + E_{xc}[\gamma]$
- <u>Note</u>: For given $\gamma(\vec{r}, \vec{r}')$ the $\{\phi_j(\vec{r}), n_j\}$ follow from diagonalization, i.e. $n_j = n_j[\gamma], \quad \phi_j = \phi_j[\gamma]$

<u>Consequence</u>: Any explicit functional $E[n_j, \phi_j(\vec{r})]$ is an implicit functional of γ

Functional Minimization

Constraints

- ★ $\sum_{i} n_i = N$, where N is the number of electrons.
- ★ $\int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d^3\mathbf{r} = \delta_{ij}$, orthonormality constraint.
- ★ $0 \le n_i \le 1$, N-representability constraint, guarantees that γ comes from an <u>ensemble</u> of fermionic many-body wavefunctions.

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- ★ $0 \le n_i \le 1$, N-representability constraint, guarantees that γ comes from an <u>ensemble</u> of fermionic many-body wavefunctions.
- The first two are enforced through Lagrange multipliers. The quantity to minimize becomes:

$$\mathcal{F} = E_{tot} - \mu \left(\sum_{i} n_{i} - N \right) - \sum_{ij} \epsilon_{ij} \left(\left\langle \phi_{i} \middle| \phi_{j} \right\rangle - \delta_{ij} \right)$$

 μ : chemical potential.



N-representability condition $0 \le n_j \le 1$ generally leads to <u>border</u> <u>minimum</u>.

i.e. one can still minimize but $\frac{\partial F}{\partial n_j} \neq 0$ at minimum

Total-energy functional:

$$E_{tot}[\gamma] = E_{kin}[\gamma] + \int V_{ext}(\vec{r})\gamma(\vec{r},\vec{r})d^{3}r + E_{H}[\gamma] + E_{xc}[\gamma]$$

4 major differences to DFT:

• Kinetic-energy functional is known <u>exactly</u>

$$E_{kin} = \int d^{3}r \int d^{3}r' \,\delta(\vec{r} - \vec{r}') \left(-\frac{\nabla^{2}}{2}\right) \gamma(\vec{r}, \vec{r}')$$
$$= \sum_{j=1}^{\infty} n_{j} \left\langle \phi_{j} \right| - \frac{\nabla^{2}}{2} \left| \phi_{j} \right\rangle$$

Hence $E_{xc}[\gamma]$ does not contain any kinetic contributions, and therefore there is no adiabatic connection and no coupling-constant-integration formula for E_{xc} . • The energy minimum is not necessarily a stationary point because minimum may be on the border, i.e. there exists **<u>no</u>** variational equation $\frac{\delta F[\gamma]}{\delta \gamma(\vec{r},\vec{r}')} = 0$

• There is <u>no</u> HK-like 1-1 correspondence between the 1-RDM and non-local external potentials $\gamma(\vec{r}, \vec{r}') \leftrightarrow v(\vec{r}, \vec{r}')$ (proof by counter example).

There exists <u>no</u> Kohn-Sham system reproducing the interacting γ(r
, r
'), because the non-interacting (KS)
 1-RDM is idempotent while the interacting one is not.



Hartree term

$$E_{H}[\gamma] = \frac{1}{2} \sum_{j,k} \mathbf{n}_{j} \mathbf{n}_{k} \int d^{3}r d^{3}r' \frac{\phi_{j}(\vec{r}) \phi_{j}^{*}(\vec{r}) \phi_{k}(\vec{r}') \phi_{k}^{*}(\vec{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Approximation for the xc energy functional

$$E_{xc}[\gamma] = -\frac{1}{2} \sum_{j,k} \sqrt{n_j n_k} \delta_{\sigma_j \sigma_k} \int d^3 r d^3 r' \frac{\phi_j(\vec{r}) \phi_j^*(\vec{r}') \phi_k(\vec{r}') \phi_k^*(\vec{r})}{|r - r'|}$$

A.M.K. Müller, Phys. Lett. <u>105</u>A, 446 (1984)

$$E_{H}[\gamma] = \frac{1}{2} \sum_{j,k} \mathbf{n}_{j} \mathbf{n}_{k} \int d^{3}r d^{3}r' \frac{\phi_{j}(\vec{r}) \phi_{j}^{*}(\vec{r}) \phi_{k}(\vec{r}') \phi_{k}^{*}(\vec{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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Self-interaction correction by S. Goedecker, C.J. Umrigar, Phys. Rev. Lett. <u>81</u>, 866 (1998)

$$E_{H}[\gamma] = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}} n_{j} n_{k} \int d^{3}r d^{3}r' \frac{\phi_{j}(\vec{r}) \phi_{j}^{*}(\vec{r}) \phi_{k}(\vec{r}') \phi_{k}^{*}(\vec{r}')}{|r - r'|}$$

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The BBC functionals

- Hierarchy of corrections to the Müller functional
- key idea: Distinction between strongly and weakly occupied orbitals
 - BBC1: Sign change of *f*, if both orbitals are weakly occupied:

$$f(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j}, & i, j \text{ weakly occupied,} \\ \sqrt{n_i n_j}, & \text{otherwise.} \end{cases}$$

• BBC2: Additionally, omission the square root if both orbitals are strongly occupied:

$$f(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j}, & \text{for } i, j \text{ weakly occupied,} \\ n_i n_j, & \text{for } i, j \text{ strongly occupied,} \\ \sqrt{n_i n_j}, & \text{otherwise.} \end{cases}$$

 BBC3: Inclusion of anti-bonding in the list of strongly occupied orbitals. Removal of SI terms.

O. Gritsenko, K. Pernal, E.J. Baerends, JCP 122, 204102 (2005).

Many approximations have the form

$$E_{xc}[\gamma] = -\frac{1}{2} \sum_{j,k} \quad \mathbf{f}(\mathbf{n}_j, \mathbf{n}_k) \quad \int d^3r d^3r' \frac{\phi_j(\vec{r}) \phi_j^*(\vec{r}') \phi_k(\vec{r}') \phi_k^*(\vec{r})}{|\mathbf{r} - \mathbf{r}'|}$$

"power functional" $f(n_j, n_k) = (n_j n_k)^{\alpha}$

S. Sharma, J.K. Dewhurst, N.N. Lathiotakis , E.K.U.G., Phys. Rev. B (Rapid Comm.) <u>78</u>, 201103 (2008) N.N. Lathiotakis, S. Sharma, J.K. Dewhurst, F. Eich, M.A.L. Marques, E.K.U.G., Phys. Rev. A (Rapid Comm.) <u>79</u>, 040501 (2009)

 $\alpha = 1$ leads to Hartree-Fock $\alpha = \frac{1}{2}$ Müller functional

Müller functional overcorrelates, HF has no correlation α can be viewed as "mixing parameter"

★ G2/97 test set of molecules [1]:

148 neutral molecules including 29 radicals, 35 non-hydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons and 15 inorganic hydrides.

★ Cartesian 6-31G* Gaussian basis-set

L.A. Curtiss et al., JCP 106, 1063 (1997); ibid. 109, 42 (1998).







N.N. Lathiotakis, S. Sharma, N. Helbig, J.K. Dewhurst, M.A.L. Marques, F. Eich, T. Baldsiefen, A. Zacarias, E.K.U.G., Zeitschrift für Physikalische Chemie <u>224</u>, 467 (2010)

<u>Ultimate goal</u>: Ab-initio treatment of "strongly correlated systems"

Chemists' paradigm: H₂ dissociation



Chemists' paradigm: H₂ dissociation



For large internuclear separation, RDMFT beats HF, DFT (LDA/GGA) and scGW.

HOW COME??

For large internuclear separation, the occupation numbers of the bonding and anti-bonding NOs become 50%-50%, i.e. the explicit dependence on the occupation numbers allows RDMFT to deal with degeneracies and near-degeneracies. **Paradigm of strongly correlated solid: Mott insulator**

Experimentally, Mott insulators are materials which, at low temperatures, are antiferromagnetic insulators that stay insulating when heated above the Néel temperature.

<u>Prototype</u>: periodic chain of equidistant hydrogen atoms without magnetic order

KS system: 1 electron per unit cell, half-filled band → metallic (independent of xc functional)

<u>formally no problem</u>: Density of a metallic KS system can reproduce density of real-world insulator

true gap:
$$\Delta = \Delta_{KS} + \Delta_{xc}$$

Kohn-Sham system very different from the true system

Side remark on periodic solids:

The 1-RDM of a metal can always be distinguished from the 1-RDM of an insulator

<u>Metal</u>: $\gamma(r,r')$ decays <u>algebraically</u> for large |r-r'|

<u>Insulator</u>: γ(r,r') decays <u>exponentially</u> for large |r-r'| decay constant is proportional to the gap

The Fundamental Gap

 $E(M) \equiv$ ground-state energy of M-electron system

For fractional particle number M, $N_0 < M < N_0 + 1$ (with N_0 integer), the correct definition of E(M) follows from the low-temperature limit of a grand-canonical ensemble

$$E(M) = \sum_{N \in \mathbb{N}} w_N \cdot E(N) \qquad M = \sum_{N \in \mathbb{N}} w_N \cdot N$$

For Coulomb systems E(N) is <u>upward convex</u> (Lieb's conjecture). This implies

$$E(N_0 + \omega) = (1 - \omega)E(N_0) + \omega E(N_0 + 1) \quad \text{for } 0 \le \omega \le 1$$



Ionization potential:

$$I(N) \equiv E(N-1) - E(N)$$

Electron affinity:

$$A(N) \equiv E(N) - E(N+1)$$

Fundamental gap:

$$\Delta \equiv I(N) - A(N)$$

(for charge-neutral N-electron system)

for periodic solids: $\Delta =$ fundamental gap

for finite systems:
$$\frac{\Delta}{2}$$
 = chemical hardness



Chemical potential:

$$\mu(M) \equiv \frac{\partial E(M)}{\partial M} = \begin{cases} -I(N) & : & N-1 < M < N \\ -A(N) & : & N < M \le N+1 \end{cases} \text{ has a jump at } M = N$$

$$\Delta = -A(N) + I(N) = \mu(N + \eta) - \mu(N - \eta)$$

In DFT:

$$\Delta = \in \underbrace{\mathsf{LUMO}}_{\text{LUMO}} (N) - \in \operatorname{HOMO}_{\text{HOMO}} (N) + \underbrace{[v_{xc} (N + \eta) - v_{xc} (N - \eta)]}_{\Delta_{KS}}$$

Discontinuity of $\mu(M)$ for the LiH molecule



The discontinuity of $\mu(M)$ at N=4 electrons for LiH

Discontinuity of $\mu(M)$ for the LiH molecule



The discontinuity of $\mu(M)$ at N=4 electrons for LiH

Fundamental gap of semiconductors and insulators

S. Sharma, J.K. Dewhurst, N.N. Lathiotakis and E.K.U.G., Phys. Rev. B 78 (Rapid Comm.), 201103 (2008)



- Thanks

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solids



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What's next?

• Finite-temperature RDMFT:

<u>Goal</u>: Ab-initio calculation of the phase diagram of strongly correlated solids

• Real-time dynamics of coupled electron-phonon system in terms electronic and phononic 1RDMs:

<u>Goals</u>: Ab-initio description of decoherence, thermalization, and laser-induced phase transitions

• Construct novel GF-functionals in the RDMFT way: $E_{xc}[G] = E_{xc}[n_j(\omega), \phi_j(r,\omega)]$

where $\int G(\vec{r},\vec{r}',\omega) \phi_j(\vec{r}',\omega) d^3r' = n_j(\omega)\phi_j(\vec{r},\omega)$