Nuclear Density Functional Theory

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Density Functional Theory in Electronic Structure Theory

For an isolated A-electron atomic or molecular system in the Born-Oppenheimer, non-relativistic approximation, the Hamiltonian is [1]

$$\hat{H} = \hat{T} + \sum_{i=1}^{A} \hat{v}_{ext}(\boldsymbol{r}_i) + \sum_{ij} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{1}$$

- We neglect the spin degree of freedom for sake of simplicity; there is no isospin in chemistry;
- $\hat{V}_1 \equiv \hat{v}_{ext}(\boldsymbol{r}_i)$ is the one-body potential representing the nucleus-electron Coulomb attraction;
- $\hat{V}_2 \equiv \frac{e^2}{4\pi\epsilon_0}/|\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the two-body potential representing the electron-electron repulsion.

In other words, the full A-body Hamiltonian is *completely known*, and only involves two-body potentials. Eigenstates of the Hamiltonian, however, are still A-body wave functions!

As usual, $|\Phi\rangle$ refers to a Slater determinant of single-particle wave-functions $\phi_a(\boldsymbol{r})$. Note: no spin or isospin degree of freedom so far since (i) there is only one type of electrons (ii) the electronic Hamiltonian does not depend on spin operators.

Applying the variational principle on the expectation value of the Hamiltonian on a Slater determinant yields

- Nuclear structure formulation

$$E = \sum_{ab} t_{ab}\rho_{ba} + \frac{1}{2}\sum_{abcd}\bar{v}_{abcd}\rho_{ca}\rho_{db} = \sum_{ab} t_{ab}\rho_{ba} + \sum_{ab}\Gamma_{ab}\rho_{ba}, \quad (2)$$

- Quantum chemistry formulation

$$E = \sum_{a=1}^{A} H_a + \frac{1}{2}\sum_{ab=1}^{A}(J_{ab} - K_{ab}); \quad (3)$$

Definitions

- One-body potential

$$H_a = \int d^3\boldsymbol{r} \; \phi_a^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m} \hat{\boldsymbol{\nabla}}^2 + \hat{v}_{\text{ext}}(\boldsymbol{r}) \right) \phi_a(\boldsymbol{r}); \qquad (4)$$

- Direct (Hartree) term

$$J_{ab} = \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_1)\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2); \quad (5)$$

- Exchange (Fock) term

$$K_{ab} = \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\phi_a(\boldsymbol{r}_2)\phi_b^*(\boldsymbol{r}_2).$$

$$(6)$$

Claim: *The external potential $\hat{v}_{ext}(\boldsymbol{r})$ is (to within a constant) a unique functional of the* local *density $\rho(\boldsymbol{r})$*; since, in turn $\hat{v}_{\text{ext}}(\boldsymbol{r})$ fixes the Hamiltonian $\hat{H}$, we see that the exact many-particle ground state is a *unique* functional of $\rho(\boldsymbol{r})$, $\rho \Leftrightarrow |\Psi\rangle$.

We can rewrite the energy of the system as

$$E[\rho] = E_{Ae}[\rho] + T[\rho] + E_{ee}[\rho] = \int d^3\boldsymbol{r}\ \hat{v}_{\text{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + F_{HK}[\rho], \quad (7)$$

with

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho]. \quad (8)$$

Here, $T[\rho]$ is the kinetic energy of the many-body system of interacting electrons (not just the sum of individual kinetic energies since the system is correlated); the potential energy $E_{ee}[\rho]$ comes from electron-electron Coulomb interactions.

Proof of the HK Theorem

It is obvious that $\hat{v}(\boldsymbol{r})$ determines the full Hamiltonian (since kinetic energy and two-body operators are fixed), hence the exact many-body wave function $|\Psi\rangle$ and the one-body local density ρ.

The HK states that the opposite is true: the density ρ of the system fixes the external potential hence $|\Psi\rangle$ [1, 2].

Proof *(ad absurdum)*
In the following, $\hat{W}$ is the two-body e-e interaction potential

$$\exists(\hat{v}_1, \hat{v}_2)/\begin{cases} \hat{v}_1 \Rightarrow (|\Psi_1\rangle, \rho),\ \hat{H}_1 = \hat{T} + \hat{v}_1 + \hat{W},\ \hat{H}_1|\Psi_1\rangle = E_1|\Psi_1\rangle \\[2mm] \hat{v}_2 \Rightarrow (|\Psi_2\rangle, \rho),\ \hat{H}_2 = \hat{T} + \hat{v}_2 + \hat{W},\ \hat{H}_2|\Psi_2\rangle = E_2|\Psi_2\rangle \end{cases}$$

Since $|\Psi_i\rangle$ is the g.s. wave function of $\hat{H}_i$, we must have

$$\begin{cases} E_1 < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle = E_2 + \langle\Psi_2|\hat{H}_2 - \hat{H}_1|\Psi_2\rangle, \\[2mm] E_2 < \langle\Psi_1|\hat{H}_2|\Psi_1\rangle = E_1 + \langle\Psi_1|\hat{H}_1 - \hat{H}_2|\Psi_1\rangle, \end{cases}$$

Since $\hat{H}_2 - \hat{H}_1 = \hat{v}_2 - \hat{v}_1$ is a one-body potential, its expectation value on $|\Psi_i\rangle$ is given by the trace with the density matrix, which is the same for both $|\Psi_1\rangle$ and $|\Psi_2\rangle$. Hence we arrive at

$$\langle\Psi_2|\hat{v}_2 - \hat{v}_1|\Psi_2\rangle = \int d^3\boldsymbol{r}\rho(\boldsymbol{r})[\hat{v}_2(\boldsymbol{r}) - \hat{v}_1(\boldsymbol{r})] \Rightarrow E_1 + E_2 < E_2 + E_1 \qquad (9)$$

Comments

The functional $F_{HK}[\rho]$ is unknown; finding it is the main challenge in electronic structure theory.

Since F_{HK} is unique (or universal), it applies equally to simple systems such as the Hydrogen atom and complex systems such as biological molecules like DNA.

One may view the Hohenberg-Kohn theorem as a reformulation of the quantum many-body problem: instead of searching for the correct many-body wave-function $|\Psi\rangle$ (which may be significantly different from a simple Slater determinant $|\Phi\rangle$), one searches instead for a functional of the local density.

Attention: at this point, the local density $\rho(\boldsymbol{r})$ is defined from the exact many-body wave function as

$$\rho(\boldsymbol{r}) = \int d^3\boldsymbol{r}_1 \ldots \int d^3\boldsymbol{r}_A \left|\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}, \ldots, \boldsymbol{r}_A)\right|^2. \qquad (10)$$

The second Hohenberg-Kohn theorem states that $F_{HK}[\rho]$, the unique functional that gives the exact ground state energy of the system, yields the lowest energy if and only if the *input density is the true ground state density.*

This is nothing but the application of the variational principle. The minimization of $F_{HK}[\rho]$ yields the density ρ that gives the exact g.s. energy. Even when we don't know the exact functional – always the case in practice, especially in nuclear physics as we will see later – we can try and minimize the energy obtained from some $F[\rho]$: the lower we get, the closer we are from the true solution.

Why can't we do this, then? Because the density ρ is not easy at all to get... Again, in the general case

$$\rho(\boldsymbol{r}) = \int d^3\boldsymbol{r}_1 \ldots \int d^3\boldsymbol{r}_A \, |\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}, \ldots, \boldsymbol{r}_A)|^2. \qquad (11)$$

The KS equations give a practical recipe to easily obtain the best density ρ given a certain energy functional $F[\rho]$.

Introduce a fictitious system of A *independent electrons, with the same (unknown) density ρ as the interacting system* we are interested in. For this system of A non-interacting electrons,

- The exact many-body wave function is a Slater determinant $|\Phi\rangle$ made of s.p. wave functions $\phi_a(\boldsymbol{r})$;
- The density is $\rho_S(\boldsymbol{r}) = \sum_{a=1}^{A} |\phi_a(\boldsymbol{r})|^2 = \rho(\boldsymbol{r})$ (by definition)
- The kinetic energy $T_S[\rho]$ is given by

$$T_S[\rho] = -\frac{\hbar^2}{2m} \sum_{a=1}^{A} \int d^3\boldsymbol{r} \; \phi_a^*(\boldsymbol{r}) \hat{\boldsymbol{\nabla}}^2 \phi_a(\boldsymbol{r}). \tag{12}$$

The non-trivial mathematical theorem behind this strategy is that there always exists such a mapping: $\rho \mapsto |\Phi\rangle$.

The energy functional of the *interacting* system can be written

$$F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho], \tag{13}$$

with $E_{XC}[\rho]$ the exchange-correlation energy given by

$$E_{XC}[\rho] = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]). \tag{14}$$

The last expression is the *definition* of the exchange-correlation energy; in practice, one tries to directly "invent" a functional that gives the lowest energy (because of the second HK theorem). Note that the exchange term of the HF equations is not included, since it is not a functional of the *local* density.

Recall that the total energy of the interacting system is then

$$E[\rho] = E_{Ae}[\rho] + F[\rho] = \int d^3\boldsymbol{r}\, \hat{v}_{ext}(\boldsymbol{r})\rho(\boldsymbol{r}) + F[\rho]. \tag{15}$$

The Kohn-Sham equations are obtained from the definition of the functional $F[\rho]$ by applying the variational principle

$$\text{Min}_\rho E[\rho] \Rightarrow \frac{\partial E[\rho]}{\partial \rho} = 0, \tag{16}$$

where we take advantage of the fact that $\rho = \rho_S$ by construction.

For electronic structure theory, the resulting equations take the form of a simple Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \hat{\boldsymbol{\nabla}}^2 + \hat{V}_S(\boldsymbol{r}) \right) \phi_a(\boldsymbol{r}) = \epsilon_a \phi_a(\boldsymbol{r}), \tag{17}$$

with

$$\hat{V}_S(\boldsymbol{r}) = \int d^3\boldsymbol{r'} \frac{\rho(\boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|} + \hat{V}_{XC}(\boldsymbol{r}) + \hat{v}_{\text{ext}}(\boldsymbol{r}). \tag{18}$$

Local Density and Generalized Gradient Approximations

In the local density approximation (LDA), the exchange-correlation part of the functional is written

$$E_{XC}^{LDA}[\rho] = \int d^3\boldsymbol{r} \; \rho(\boldsymbol{r})\epsilon_{XC}[\rho(\boldsymbol{r})]. \tag{19}$$

This expression is extended in the generalized gradient approximation (GGA), by

$$E_{XC}^{GGA}[\rho(\boldsymbol{r},\boldsymbol{r'})] = \int d^3\boldsymbol{r} \; \epsilon_{XC}[\rho(\boldsymbol{r},\boldsymbol{r'}), \boldsymbol{\nabla}\rho(\boldsymbol{r},\boldsymbol{r'})]. \tag{20}$$

The GGA amounts to introducing functionals of the *non-local one-body density matrix*, instead of restricting oneself to functional of the local density (technically the diagonal term of the full one-body density matrix).

Going Further

There exist extensions of the Hohenber-Kohn theorems and Kohn-Sham equations for (i) spin-polarized systems (ii) excited states, (iii) density operators (statistical quantum mechanics).

The DFT equations of electronic structure theory are often solved on a basis of states upon which the KS orbitals are expanded. This is the spirit of the linar combination of atomic orbitals (LCAO) technique. Some of the bases used are (i) Slater-type-orbitals (STO), (ii) Gaussian-type-orbitals (GTO), contracted Gaussian functions (GTF), etc.

The two main technical difficulties in solving the DFT equations:

- The Coulomb potential has a finite range and a singularity at $r = 0$
- Contrary to the harmonic oscillator used abundantly in nuclear physics, bases may not be orthonormal, orthogonal or even complete.

Energy Density Functional Formalism

Remember that the Skyrme HF interaction energy could be recast into

$$E_{\text{int}} = \int d^3 \boldsymbol{r} \sum_{t=0,1} \chi_t(\boldsymbol{r}) \tag{21}$$

with $\chi(\boldsymbol{r})$ the *energy density functional* (EDF).

This is very reminiscent of the generalized gradient approximation of density functional theory:

- The energy is the integral over space of some energy density;
- The energy density is a functional of the non-local one-body density matrix and its derivatives.

The energy density functional (EDF) approach to nuclear structure builds upon this analogy with electronic DFT. It is a general technique to solve the quantum many-body problem of A nucleons in interaction.

There are several *essential* differences between electronic DFT and the nuclear EDF theory:

- Nuclear forces involve two-, three-, up to A-body terms. Their analytical form is largely unknown, but they are presumed to be highly non-local (in coordinate and momentum space). By contrast electron-electron interactions are two-body only, local, and are perfectly known. While DFT is "only" a remapping of the quantum many-body problem for a *known* Hamiltonian, the nuclear EDF approach is based on a similar remapping with an *unknown* Hamiltonian.

- Spin degrees of freedom are essential, even for non-polarized nuclei such as even-even systems.

- There are two types of nucleons, protons and neutrons, hence the need for isospin degrees of freedom. This extra quantum numbers may add significant technical and even conceptual complications, for example in $N = Z$ nuclei.

- Electrons are bound by a lattice of ions in a molecule, or around a central nucleus in an atom. There is no such external potential for nuclei, which are self-bound. Consequence: the electron density $\rho(\boldsymbol{r})$ is expressed in the *laboratory frame*, defined by the lattice; the nucleon densities, $\rho_n(\boldsymbol{r})$ and $\rho_p(\boldsymbol{r})$ are defined in the *intrinsic frame* of the nucleus: $\boldsymbol{r}$ has a different meaning in the two cases. There have been attemps to generalize the HK theorem and KS techniques in this case [3].
- Because nuclei are both finite and self-bound, several symmetries of the nuclear Hamiltonian are spontaneously broken. The best example is translational invariance: nuclei are localized in space, even though nuclear forces are translationally invariant. Other symmetries that are very often broken: particle number, rotational invariance, parity, time-reversal invariance. The concept of symmetry breaking and of symmetry restoration is fundamental in nuclear structure.

The EDF approach is based upon the Hartree-Fock-Bogoliubov approximation to the many-body problem [4, 5].

In its single-reference (SR) formulation, it relies on the following assumptions:

- Starting from a s.p. basis $(c_m^\dagger, c_n)$ of the Hilbert space, we introduce the Bogoliubov transformation $\mathcal{W}$ and the quasiparticle vacuum $|0\rangle$, which will represent the ground-state of the nucleus in the EDF approach;
- The one-body density matrix ρ, the pairing tensor κ and its complex conjugate κ^* are the degrees of freedom of the theory;
- Auxiliary *local* densities such as s, τ, $\mathbb{J}$, j, T, etc., are derived from ρ (and in principle κ) by taking derivatives up to order n [6];
- Local *energy kernels* $\chi(r)$ are constructed from local densities by forming all possible p-linear ($p = 2$ usually) combinations of local densities that are scalar, time-even, and isoscalar [6, 7].

In the SR-EDF approach without proton-neutron mixing, the energy of the nucleus thus takes the general form

$$E[\rho, \kappa, \kappa^*] = \int d^3 r \left\{ \mathcal{E}_{\rho\rho}(\boldsymbol{r}) + \mathcal{E}_{\kappa\kappa}(\boldsymbol{r}) \right\}, \qquad (22)$$

where $\mathcal{E}_{\rho\rho}(\boldsymbol{r})$ corresponds to the particle-hole channel (it includes the kinetic energy density) and $\mathcal{E}_{\kappa\kappa}(\boldsymbol{r})$ to the particle-particle channel.

The density matrix and pairing tensor are obtained as usual from the solutions to the HFB equations. The latter require the mean-field h and pairing field Δ; in configuration space,

$$h_{mn} = \frac{\partial E}{\partial \rho_{nm}}, \quad \Delta_{mn} = \frac{\partial E}{\partial \kappa^*_{mn}}. \qquad (23)$$

EDF and DFT

As outlined above, the EDF approach does not introduce any specific interaction potential $\hat{V}$, only an energy density formed out of local densities.

This implies that:

- The Pauli principle is not necessarily satisfied. In fact it is violated as soon as the energy density is *not* derived from the HFB expectation value of a pseudopotential, thus implying that

  - Formally, $\mathcal{E}_{\rho\rho}$ and $\mathcal{E}_{\kappa\kappa}$ are different (think of the simple pairing forces compared to Skyrme functionals);
  - Non-local exchange terms have been dropped out or approximated by some functional of the local density: for example, Coulomb exchange terms are rarely computed exactly, see next slide.

- All *many-body correlations* should be included in the energy densities $\mathcal{E}_{\rho\rho}$ and $\mathcal{E}_{\kappa\kappa}$.

Recall that, in the Kohn-Sham scheme, the density is

$$\rho(\boldsymbol{r}) = \sum_{a=1}^{A} |\phi_a(\boldsymbol{r})|^2. \tag{24}$$

Often in DFT, the non-local exchange contribution to the energy is computed at the Slater approximation

$$E_{\text{Cou}}^{(\text{exc})}[\rho_p] = -\frac{3e^2}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3\boldsymbol{r}\ \rho_{\text{p}}^{4/3}(\boldsymbol{r}). \tag{25}$$

What happens if $A = 1$? There is a non-zero exchange interaction energy of an electron with himself... This spurious, clearly non-physical effect is called the *self-interaction* [1].

Direct phenomenological constructions of the EDF are plagued with self-interaction energies.

If the EDF can be obtained by taking the expectation value of some Hamiltonian $\hat{H} = \hat{T} + \hat{V}$ on the qp vacuum, we get

$$E[\rho, \kappa, \kappa^*] = \sum_{ab} t_{ab}\rho_{ba} + \frac{1}{2}\sum_{abcd}\bar{v}_{abcd}\rho_{ca}\rho_{db} + \frac{1}{4}\sum_{abcd}\bar{v}_{abcd}\kappa^*_{ab}\kappa_{cd} \quad (26)$$

If the potential $\hat{V}$ is zero-range, then this energy can be expressed as the integral over space of the energy density, which only depends on local densities (the Skyrme-type EDF).

When such an EDF is derived from a genuine potential (without density dependence), and all exchange contributions to the energy are taken into account then,

- The Pauli principle is verified ($\bar{v}_{aaaa} = 0$ automatically), see [8] for the proof in the HF case;
- There is no self-interaction or self-pairing.

Comparison EDF versus Pseudopotentials

EDF	Pseudopotential
No Hamiltonian implies that *all* calculations should be performed at the HFB level	Well-defined potential $\hat{V}$ implies that various approximation levels are possible and needed: HF, HFB, RPA, GCM, etc.
Pauli principle is probably not respected	Pauli principle is respected if the potential is density independent
Self-interaction and self-pairing are almost unavoidable	Self-interaction and self-pairing are irrelevant
Bridge with theory of nuclear forces	How to include correlations is well-known

Why Bother with EDF?

Remember: We introduced pseudopotentials (aka effective forces) in order to be able to work with "simple" reference states $|\Phi\rangle$.

Skyrme and Gogny pseudopotentials have proved very useful, but they do not give the kind of accuracy and precision needed today: deviations with masses is of the order of 1 MeV unless phenomenological corrections are added.

Such effective pseudopotentials do not really provide a path to improve the predictive power of the theory: how can we relate them with the theory of nuclear forces?

Today, the only answer is based on applying the density matrix expansion on (more) realistic potentials: this mechanism automatically yields an EDF and not a Hamiltonian.

Energy density functionals are the bridge between structure of heavy nuclei and the theory of nuclear forces.

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