Computational Physics Course 2018 summer

Brief introduction of lecturers

Profs. Sugino and Arita will cover the density functional theory of the electronic structure of materials. Sugino belongs to the Institute of Solid State Physics (ISSP) and working mainly on the understanding and prediction of interfaces, nanomaterials, and biomaterials. Arita belongs to RIKEN and working on the strongly correlated electrons in a material. We will introduce emerging field of the combined density functional theory and many-body theory.

Schedule

In the first half of the course (until the end of June 4), the lectures are given by Prof. Sugino. The lecture includes practice of simulation using the software package "Quantum Espresso". The contents are

1. Density functional theory (DFT)
2. Density functional Linear response theory; static and dynamical
3. Many-body perturbation theory and DFT
4. Dynamics

In the second half (from June 11), the lectures are given by Prof. Arita. The contents are

1. Dynamical mean field theory and the extensions
2. Combination of dynamical mean field and density functional theory
3. Introduction of recent studies

Plan of the first half ---Density functional theory (DFT) and simulation--- by Sugino

This document includes the contents of the lectures given in the first half part of the course.

General introduction

The purpose of this lecture (the first half) is to introduce students the density functional theory (DFT) and its extensions developed as a tool to simulate the electronic structure of materials and to predict properties of materials. The importance of DFT is in the practicality; the theory provides an approximate but practical way to understand the electronic structure, which has had, and will continue to have, impact in the research of materials. (In my definition, materials mean those matters targeted by condensed matter physics, biophysics, or chemical physics.) In this context, I consider it important for beginners to practice a simulation, so that students are requested to do a few simulations for the report assignment.

Why is the practicality so important?

As will be shown in the lecture, the electronic structure can be understood via the wave function, or alternative ones such as the Green's function. The many-body wave function, however, has so large degrees of freedom that the amount of the information is already close to "infinity" even for a ten electron system. This may be understood by counting the number of ways to assign ten electrons to M orbitals, which amounts to M^{10}! Although the number can be effectively reduced in a direct and straightforward way according to the recent information theory --- which indicates that we do not have to explore the whole Hilbert space ---, the wave function may not be a convenient tool to access the electronic structure except for very indispensable situations. The need for practical theory has lead to the invention (development) of the density functional theory. This point was emphasized by W. Kohn in his Nobel prize lecture.

The invent of DFT was turned out to be revolutionary in that the electronic structure calculation has made the easy access of nonexperts, including experimentalists and theoreticians working on abstract models. From a practical point of view, I hear that experimentalists are often required to do a DFT simulation to support the experiment by reviews of scientific journals and similar things happen for the abovementioned theoreticians. It will be better not to learn DFT simulation after the requirement but to do that beforehand. Experiencing a simulation at the start of his/her research life should be advantageous.

Simulation in this course

I will spend an hour or more to provide students how to install a simulation software and how to use it. I will focus on the program package called Quantum Expresso (QE). This is because this is, at present, one of the most popular one in the world and there are many how-to's can be found on the internet. Students are requested to use their own laptop PC and are guided to do a few simulations and are requested to report the results. The target of the simulation will be carefully chosen to avoid too long simulation on the laptop PC: This necessarily mean that the most of the advanced simulations are excluded from the exercise. Nevertheless, the basic simulations required in the course will help imagine how the advanced one may be attacked when a supercomputer is available.

At the beginning of the first half

In this context, I will begin by introducing DFT and explaining how to install QE. This early stage will take a few days in the course (during April).

Introduction to Density functional theory (DFT)

I will follow the article written by J. Toulouse
http://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_dft.pdf
which was prepared for the summer school in France.

Some recommended articles

The most popular introduction to DFT was written by Parr and Yang.

R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules (Oxford University Press, New York, 1989).

which covers the development until mid-1980. Practical aspect of DFT simulation is summarized in

W. Koch and M. C. Holthausen, A Chemist's Guide to Density Functional Theory (Wiley-VCH, New York, 2001),

which covers the technology on the exchange-correlation that had been developed until 2000 although further developments were made thereafter. Most recent textbook can be found, for example, in

T. Helgaker, P. Jørgensen and J. Olsen, Density–Functional Theory: A Convex Treatment (WileyBlackwell, 2016)

The starting Hamiltonian

For the moment, we rely on the Born-Oppenheimer approximation and non-relativistic approximation for N-electron systems. (Note that these approximations are not valid in recent high-accuracy simulations but they provide an important starting point for the simulations, as may be explained later in this course). Then, the target of study is the electronic Hamiltonian, consisting of the kinetic energy of electrons, electron-electron interaction, and the Coulomb field from the nuclear charge

$$\hat{H}_{\mathrm{el}} = \hat{T}_{\mathrm{el}} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}, \tag{1.4}$$

for the details see Eqs. (1.1)-(1.4) of the article by J. Toulouse (hereafter, I will call it just "article"). Instead of the wave function $|\Psi\rangle$, the density $n(\boldsymbol{r})$ can be used to characterize the ground state: This is what DFT is telling about.

What does it mean?

The density is defined by

$$n(\boldsymbol{r}) = N \iiint |\Psi(\boldsymbol{x}, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N)|^2 \, d\sigma d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_N \tag{1.6}$$

where $\boldsymbol{x}$ is the space-spin coordinate, and satisfies $\int n(\boldsymbol{r}) d\boldsymbol{r} = N$. This three-dimensional quantity is the "descriptor" of the N-electron system although $|\Psi\rangle$ is, of course, the descriptor as well. This surprising statement was shown by Hohenberg and Kohn about fifty years ago. (This is surprising when considering large difference in the degrees of freedom between the density and the wave function.)

Hohenberg-Kohn theorem

This theorem can be understood in terms of the "mapping" of the electron density $n(\boldsymbol{r})$ from/to the potential from the nuclear charge, which is generalized as an external potential $v(\boldsymbol{r})$. In considering the mapping, it is trivial that mapping from v to n exits simply because, given the external potential v, one can solve, in principle, the Schrödinger equation and the density n is obtained from Eq. (1.6). What is nontrivial is the reverse mapping, i.e., mapping from n to v, which can be derived as follows. (Before going in detail on the Hohenberg-Kohn theorem, I note that this may be counterintuitive in that the precise measurement of the electron density yields uniquely the position of nuclei.)

The proof can be given by different ways; (1) two-step proof by contradiction and (2) proof using the Levy's constraint search. Here I will show the first one only.

Two-step proof by contradiction (a modified version)

We will derive a contradiction for the assumption that there exist two local potentials (differing by more than an additive constant) which have the same ground-state density.

From the two local potentials, $v_1(\boldsymbol{r})$ and $v_2(\boldsymbol{r})$ which differ more than an additive constant, one can construct the Hamiltonians, $\hat{H}_1 = \hat{T} + \hat{W}_{ee} + \hat{V}_1$ and $\hat{H}_2 = \hat{T} + \hat{W}_{ee} + \hat{V}_2$. Let us assume that they share the same ground state $|\Psi\rangle$. Then, one gets

$$(\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle, \tag{1.9}$$

namely

$$\sum_{i=1}^{N}[v_1(\boldsymbol{r}_i) - v_2(\boldsymbol{r}_i)]\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = (E_1 - E_2)\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N). \tag{1.10}$$

holds globally in the phase space, leading to $v_1(\boldsymbol{r}) - v_2(\boldsymbol{r}) = \text{const}$ when the potentials reasonably well behave almost everywhere so that $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) \neq 0$ except for some points. This contradicts with the initial hypothesis.

We will then assume that different states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ corresponding to $\hat{H}_1$ and $\hat{H}_2$, respectively, have the same density $n(\boldsymbol{r})$. Since the states are different and therefore $|\Psi_2\rangle$ cannot be a ground-state wave function of $\hat{H}_1$,

$$E_1 = \langle\Psi_1|\hat{H}_1|\Psi_1\rangle < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle = \langle\Psi_2|\hat{H}_2 + \hat{V}_1 - \hat{V}_2|\Psi_2\rangle = E_2 + \int [v_1(\boldsymbol{r}) - v_2(\boldsymbol{r})]n(\boldsymbol{r})d\boldsymbol{r} \tag{1.11}$$

holds. In parallel, we can show the following:

$$E_2 < E_1 + \int [v_2(\boldsymbol{r}) - v_1(\boldsymbol{r})]n(\boldsymbol{r})d\boldsymbol{r} \tag{1.12}$$

Then, we arrive at an inconsistent inequality $E_1 + E_2 < E_1 + E_2$.

Therefore, we are lead to the conclusion that $v_1(\boldsymbol{r})$ and $v_2(\boldsymbol{r})$ are the same except for the additive constant and the mapping from n to v exists.

From the discussion made in the proof it is also clear that the ground-state energy E can be obtained as a minimum of the expectation value of the Hamiltonian, or there exist a total-energy functional $E[n]$ which is given as

$$E[n] = \min_n \left\{ \left\langle \Psi[n] \middle| \hat{T} + \hat{W}_{\text{ee}} + \int v[n](\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} \middle| \Psi[n] \right\rangle \right\}. \tag{1.15}$$

We can also define a functional called Hohenberg-Kohn functional as

$$F[n] = \min_n \left\{ \left\langle \Psi[n] \middle| \hat{T} + \hat{W}_{\text{ee}} \middle| \Psi[n] \right\rangle \right\}. \tag{1.14}$$

v-representability

It is reminded that $\Psi[n]$ is not uniquely determined when the ground-state is degenerate; nevertheless, F and E are unique. These values can be determined by finding a minimum once the functionals $F[n]$ and $E[n]$ are established. This, however, does not mean that the statement is of practical importance, especially because the search needs to be restricted to within those represented from the ground-state wave function via Eq. (1.6), namely those that satisfy the v-representable condition. All three-dimensional functions are not necessarily v-representable!

Levy-Lieb constrained minimization

The Hohenberg-Kohn functional $F[n]$ can be made more practical when we introduce an alternative definition (Levy and Lieb)

$$F[n] = \min_{\Psi \to n} \left\langle \Psi \middle| \hat{T} + \hat{W}_{\text{ee}} \middle| \Psi \right\rangle \tag{1.17}$$

in terms of the constrained minimization of Ψ. This should provide the same functional as that provided by Eq. (1.14) but does not require the v-representability, so that the minimum can be found by simply researching all functions that satisfy $\int n(\boldsymbol{r}) d\boldsymbol{r} = N$: namely assuming N-representability. Of course, the obtained density does not necessarily satisfy the v-representability, which needs to be checked afterwards. When Eq. (1.17) is introduced, it is straightforward to show that the ground-state energy can be obtained by minimizing $n(\boldsymbol{r})$:

$$\begin{aligned} E_0 = \min_{\Psi} \left\langle \Psi \middle| \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{en}} \middle| \Psi \right\rangle &= \min_n \min_{\Psi \to n} \left\langle \Psi \middle| \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{en}} \middle| \Psi \right\rangle \\ &= \min_n \left\{ \min_{\Psi \to n} \left\langle \Psi \middle| \hat{T} + \hat{W}_{\text{ee}} \middle| \Psi \right\rangle + \int v(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} \right\} \\ &= \min_n \left\{ F[n] + \int v(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} \right\} \qquad (1.18) \end{aligned}$$

Additional comment of Hohenberg-Kohn theorem

It should be emphasized that it has been taking about 50 years to find a reasonable functional form appropriate for materials; the accuracy is still not enough for many materials. In the early stage, people searched a form for the kinetic energy functional $T[n]$, but the efforts have not been so successful. Instead, method of Kohn-Sham was introduced as will be explained below. People have also searched a form for the electron-electron interaction, $V_{\mathrm{ee}}[n]$; equivalently, a form for the exchange-correlation functional after decomposing it as $V_{\mathrm{ee}}[n] = V_{\mathrm{H}}[n] + V_{\mathrm{xc}}[n]$, where the first term is the Hartree-energy defined as

$$V_{\mathrm{H}}[n] = \frac{1}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}d\boldsymbol{r}'.$$

Exercise

To understand the difficulty of constructing the kinetic energy functional, let us test the one constructed according to the Thomas Fermi model. According this model, the kinetic functional is given as

$$T = \frac{3^{5/3}\pi^{4/3}}{10}\int n(\boldsymbol{r})^{5/3} d\boldsymbol{r}$$

for a three-dimensional system and as

$$T = \frac{\pi^2}{6}\int_0^L dx\, n(x)^3 dx$$

for a one-dimensional system. From this, one can naively define the kinetic energy density functional as

$$t[n(x)] = \frac{\pi^2}{6} n(x)^3.$$

This is a local density approximation to the kinetic energy.

The integration can be done analytically for a 1D potential well of infinite wall height, where the wave function has a form

$$\varphi_n(x) = \sqrt{2/L}\sin\left(\frac{n\pi x}{L}\right),$$

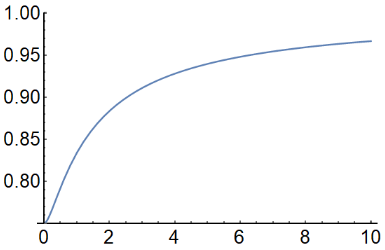
And the kinetic energy is given as

$$T = \sum_n^N \frac{2}{L}\int_0^L \frac{1}{2}\left(\frac{n\pi}{L}\right)^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{\pi^2}{6L^2} N(N+1)\left(N+\frac{1}{2}\right).$$

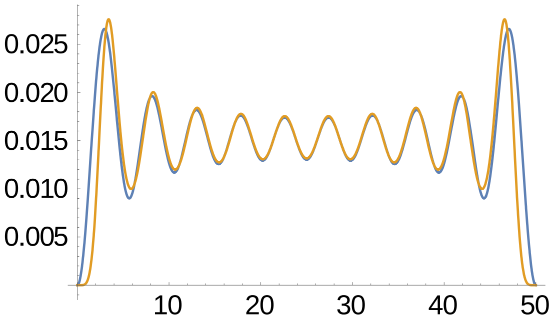
When using the Thomas Fermi model, the kinetic energy is approximated as

$$T^{\mathrm{TF}} = \frac{\pi^2}{6}\int_0^L \left\{\frac{2}{L}\sum_n^N \sin^2\left(\frac{n\pi x}{L}\right)\right\}^3 dx = \frac{\pi^2}{6L^2} N\left(N^2+\frac{9}{8}N+\frac{3}{8}\right).$$

Therefore, the ratio T^{TF}/T behaves as a function of the density N/L like



which is reasonably well for higher density, or large value for N/L, but deteriorates with decreasing density. The reason can be found by comparing the TF kinetic density and the exact one.



The values for $N=10, N/L=6$ are comparable in the region between the potential walls but are quite different near the end points. This reflects the general difficulty of constructing the kinetic energy density functional in the region where the density rather abruptly changes.

Note that the potential changes very abruptly near the nuclear position as well and the density also changes in the core region. This is the reason why Thomas Fermi model fails; the model cannot reproduce the shall structure of an atom!

Kohn-Sham method (modern version)

To overcome the problem of constructing the kinetic energy functional, Kohn and Sham proposed a method to replace the kinetic energy functional with that of a non-interacting system that share the same density $n(\boldsymbol{r})$. More precisely, one assumes there always exists a non-interacting system under the influence of an effective potential $v_{\text{eff}}(\boldsymbol{r})$ whose ground-state electron density is the same as that of the target system of interest. Since the wave function of the non-interacting system can be relatively easily computed numerically, the corresponding kinetic energy functional can also be obtained, which will be denoted as $T_s[n]$. The proposition of Kohn and Sham is to use $T_s[n]$ instead of $T[n]$ and approximate $F[n]$ as

$$F[n] = T_s[n] + V_{\mathrm{H}}[n] + V_{\mathrm{xc}}[n],$$

where

$$T_s[n] = \min_{\Phi\to n}\langle\Phi|\hat{T}|\Phi\rangle = \langle\Phi[n]|\hat{T}|\Phi[n]\rangle. \tag{1.21}$$

The last equation reflects the fact that the non-interacting system can be represented by the Slater determinant Φ. (Here we use the Hartree-Fock state as the reference system but it can be anything in principle. Importantly, the reference system should be such that the ground-state wave function can be prepared.)

By tracing Eq. (1.18) reversely, we find that the total-energy can be obtained by searching for the density representable by the Slater determinant that minimizes the HK functional as

$$\begin{aligned} E_0 = \min_n \left\{ F[n] + \int v(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} \right\} &\Rightarrow \min_n \left\{ \min_{\Phi\to n} \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathrm{Hxc}}[n] + \int v(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} \right\} \\ &= \min_n \left\{ \min_{\Phi\to n} \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[n_\Phi] \right\} \\ &= \min_\Phi \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[n_\Phi] \right\}. \end{aligned} \tag{1.22}$$

By minimizing the functional with respect to the Slater determinant Φ, the density can be obtained as n_Φ. Note that the Hartree-exchange-correlation functional can be decomposed into

$$E_{\mathrm{Hxc}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

where

$$E_{\mathrm{x}}[n] \equiv \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle - E_{\mathrm{H}}[n], \tag{1.26}$$

and

$$E_{\mathrm{c}}[n] \equiv \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle. \tag{1.27}$$

From these definition, we find that the difference in the true kinetic energy functional and that of the non-interacting system, $T[n] - T_s[n]$, is absorbed by the correlation functional and thus the correlation function is comprised of the kinetic energy contribution and potential energy contribution.

$$E_{\mathrm{c}}[n] = T_{\mathrm{c}}[n] + U_{\mathrm{c}}[n], \tag{1.27}$$

where

$$\begin{aligned} T_{\mathrm{c}}[n] &\equiv \langle \Psi[n] | \hat{T} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle \\ U_{\mathrm{c}}[n] &\equiv \langle \Psi[n] | \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle. \end{aligned}$$

Note that this is rather old definition of the exchange-correlation functional but recently the “dirty” definition, dirty in that the kinetic energy and the potential energy having different scaling properties are mixed, is avoided by introducing the adiabatic connection formula, as explained below.

Kohn-Sham equation

It is well described in many textbook on DFT how to determine the Slater determinant. It is determined by solving a Schrödinger-like equation called Kohn-Sham equation. The equation can be derived by rewriting the minimization with respect to Φ with that with respect to the constituent single-electron orbitals ψ_i. Within the scheme of the unrestricted closed-shell description of the Slater determinant, $\psi_i(\boldsymbol{x}) = \phi_i(\boldsymbol{r})\chi_{\sigma_i}(\sigma)$, the functional to be minimized is

$$E[\{\phi_i\}] = \sum_i^N \int \phi_i^*(\boldsymbol{r})\left(-\frac{\boldsymbol{\nabla}^2}{2} + v_{\mathrm{ne}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r})d\boldsymbol{r} + E_{\mathrm{Hxc}}[n] \tag{1.28}$$

which is very similar to the Hartree-Fock energy. The variation needs to be done by keeping the orthonormal condition and the relation

$$n(\boldsymbol{r}) = \sum_i^N |\phi_i(\boldsymbol{r})|^2. \tag{1.29}$$

When the variation is done using the method of Lagrange multiplier,

$$\mathcal{L}[\{\phi_i\}] = E[\{\phi_i\}] - \sum_i^N \varepsilon_i\left(\int \phi_i^*(\boldsymbol{r})\phi_i(\boldsymbol{r})d\boldsymbol{r} - 1\right), \tag{1.30}$$

as

$$\frac{\delta\mathcal{L}[\{\phi_i\}]}{\delta\phi_i^*(\boldsymbol{r})} = 0, \tag{1.31}$$

we can obtain the differential equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) + \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta\phi_i^*(\boldsymbol{r})} = \varepsilon_i\phi_i(\boldsymbol{r}). \tag{1.32}$$

The left-hand side of the equation can be rewritten as

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) + \int \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r}')}\frac{\delta n(\boldsymbol{r}')}{\delta\phi_i^*(\boldsymbol{r})}d\boldsymbol{r}' = \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r}) + v_{\mathrm{Hxc}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}).$$

Therefore, the differential equation becomes

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r}) + v_{\mathrm{Hxc}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}). \tag{1.35}$$

This is called as the Kohn-Sham equation.

Self-consistent field

Note that the effective potential $v_{\mathrm{eff}}(\boldsymbol{r}) \equiv v_{\mathrm{ne}}(\boldsymbol{r}) + v_{\mathrm{Hxc}}(\boldsymbol{r})$ is a functional of the density $n(\boldsymbol{r})$, so that the Kohn-Sham equation needs to be solved keeping self-consistency between the density used to construct the effective potential and that resulting from (1.29). This makes the calculation much more difficult than the one-electron Schrödinger equation. At this point, it is very instructive to compare the Kohn-Sham equation and the Hartree-Fock equation: The latter is

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}) + v_{\mathrm{x}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}),$$

where

$$v_{\mathrm{x}}(\boldsymbol{r})\phi_i(\boldsymbol{r}) = -\sum_{j}^{N}\int\frac{\phi_j^*(\boldsymbol{r}')\phi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\,\phi_j(\boldsymbol{r}) = -\int\frac{\sum_j\phi_j^*(\boldsymbol{r}')\phi_j(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi_i(\boldsymbol{r}')d\boldsymbol{r}'$$

$$\equiv\int v_x(\boldsymbol{r},\boldsymbol{r}')\phi_i(\boldsymbol{r}')d\boldsymbol{r}'$$

is non-local. The non-local nature of the Hartree-Fock has a significant meaning in that contributions of the i-th orbital to the Hartree potential $v_{\mathrm{H}}(\mathbf{r})$ and the exchange potential $v_{\mathrm{x}}(\boldsymbol{r},\boldsymbol{r}')$ are the same except for the different sign. That is, the contributions of the i-th orbitals are canceled out. This property of the effective potential is called self-interaction free.

Local density approximation for the exchange-correlation

The exchange-correlation functional, given by Eqs. (1.26-1.27), are non-local; non-locality of the exchange was shown explicitly in the above and that of the correlation is more complicated as shown below. Non-locality makes the self-consistent calculation very complicated. In the early stage of DFT, therefore, people searched for a local form for the exchange-correlation.

The simplest form for the exchange can be found in the literature as the Thomas Fermi exchange or Dirac exchange as

$$E_{\mathrm{x}}[n(r)] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int n(\boldsymbol{r})^{\frac{4}{3}}\,d\boldsymbol{r}. \tag{1.53}$$

Later, elaborate calculation was done for homogeneous electron gas, where the electron density is constant, using various values for the electron density n and the calculated energy density was related to n to find a better local form for the exchange-correlation. The resulting functional was called "local density approximation (LDA)". LDA was found to reasonably well reproduce the energy of many weakly interacting electrons and was used to predict stability, phonon, dynamics of materials.

How to deal with spin

You may wonder how to deal with spin. Or, you may alternatively want to use an unrestricted Hartree-Fock form for the non-interacting system (see discussion around Eq. (1.28)). The HK functional can be defined as

$$F[n_\uparrow,n_\downarrow] = \min_{\Psi\to n_\uparrow,n_\downarrow}\langle\Psi|\hat{T}+\widehat{W}_{\mathrm{ee}}|\Psi\rangle. \tag{1.57}$$

The search is done for normalized antisymmetric functions Ψ that yields

$$n_\uparrow(\boldsymbol{r}) = N\iiint|\Psi(\boldsymbol{r}\uparrow,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_N)d\boldsymbol{x}_2\cdots d\boldsymbol{x}_N \tag{1.58a}$$

and

$$n_{\downarrow}(\boldsymbol{r}) = N \iiint |\Psi(\boldsymbol{r}\downarrow, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_N. \tag{1.58b}$$

A KS scheme can be derived by decomposing $F[n_{\uparrow}, n_{\downarrow}]$ into the kinetic, Hartree, and exchange-correlation parts, where the kinetic part is defined as

$$T_s[n_{\uparrow}, n_{\downarrow}] = \min_{\Phi \to n_{\uparrow}, n_{\downarrow}} \langle \Phi | \hat{T} | \Phi \rangle. \tag{1.60}$$

The Slater determinant is composed from the one-electron orbital of the form

$$\psi_i(\boldsymbol{x}) = \phi_{i\sigma_i}(\boldsymbol{r}) \chi_{\sigma_i}(\sigma)$$

and then the KS equation can be derived separately for each spin state

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\boldsymbol{r}) + v_{\text{H}}(\boldsymbol{r}) + v_{\text{xc},\uparrow}(\boldsymbol{r})\right) \phi_{i\uparrow}(\boldsymbol{r}) = \varepsilon_{i\uparrow}(\boldsymbol{r}) \phi_{i\uparrow}(\boldsymbol{r}) \tag{1.61a}$$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\boldsymbol{r}) + v_{\text{H}}(\boldsymbol{r}) + v_{\text{xc},\downarrow}(\boldsymbol{r})\right) \phi_{i\downarrow}(\boldsymbol{r}) = \varepsilon_{i\downarrow}(\boldsymbol{r}) \phi_{i\downarrow}(\boldsymbol{r}) \tag{1.61b}$$

The exchange-correlation potentials are given in terms of the derivative with respect to the electron densities as shown in Eqs. (1.62)-(1.63) of the article. It was shown by Oliver and Perdew that the spin-dependent exchange functional $E_{\text{x}}[n_{\uparrow}, n_{\downarrow}]$ can be expressed rigorously as

$$E_{\text{x}}[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2}(E_{\text{x}}[2n_{\uparrow}] + E_{\text{x}}[2n_{\downarrow}]), \tag{1.64}$$

because, in the non-relativistic case,

$$E_{\text{x}}[n_{\uparrow}, n_{\downarrow}] = E_{\text{x}}[n_{\uparrow}, 0] + E_{\text{x}}[0, n_{\downarrow}] \tag{S.8}$$

holds and, therefore, when using the spin-unpolarized case, $n_{\uparrow} = n_{\downarrow} = n/2$, we get

$$E_{\text{x}}[n, 0] = E_{\text{x}}[0, n] = \frac{1}{2} E_{\text{x}}[2n]. \tag{S.9}$$

using the spin-scaling relation which states that the up-spin density and down-spin density are uncoupled to form the exchange functional.

This formalism for the spin density functional theory suggests a possibility to construct extended formalisms as well. Indeed, by describing the HK functional in terms of the density and the current density, the current density functional theory was developed and was applied to electrons under excited states. One can also describe the HK functional using the electric field and magnetic flux to simulate the electrons under inhomogeneous electromagnetic field. In those cases, it is not obvious if one can prepare appropriate exchange-correlation functional. If one wants to follow the procedure adopted in LDA, one needs to do an accurate simulation under the inhomogeneous conditions and establish the functional relation. This is not always possible especially when one needs to construct a non-local functional for accuracy.

Density matrix formalism

As a step to extend LDA, it is convenient to adopt the density matrix formalism or the Green's function formalism. Let us, for the moment, focus on the former formalism. In that case, we need to investigate up to the second order density matrix because we are studying electrons interacting through two-body interaction, that is the Coulombic interaction.

The two-body density matrix is defined as

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = N(N-1) \iiint |\Psi[n](\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N)|^2 d\sigma_1 d\sigma_2 d\boldsymbol{x}_3 \cdots d\boldsymbol{x}_N, \tag{2.1}$$

although factor 1/2 is multiplied in many literatures. This corresponds to the probability of finding two electrons simultaneously at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. This density matrix is particularly important because the electron-electron interaction functional can be written using n_2 as

$$\langle \Psi[n] | \widehat{W}_{\mathrm{ee}} | \Psi[n] \rangle = \frac{1}{2} \iint \frac{n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2. \tag{2.2}$$

The two-body density matrix is conventionally decomposed into the product of the density and the rest as

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = n(\boldsymbol{r}_1) n(\boldsymbol{r}_2) + n_{2,\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{2.3}$$

The second term in the right-hand side is called the exchange-correlation pair density, which can be further decomposed as

$$n_{2,\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = n(\boldsymbol{r}_1) n_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{2.4}$$

where n_{xc} is called the exchange-correlation hole. We call this as a hole because of the existence of the following sum rule

$$\int n_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_2 = -1. \tag{2.6}$$

That is, the value is negative when integrated over the whole space. The electron-electron interaction energy can be rewritten as

$$\langle \Psi[n] | \widehat{W}_{\mathrm{ee}} | \Psi[n] \rangle = \frac{1}{2} \iint \frac{n(\boldsymbol{r}_1) n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 + \frac{1}{2} \iint \frac{n(\boldsymbol{r}_1) n_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2.$$

This indicates that the (potential energy contribution) of exchange-correlation energy is given by the interaction with its exchange-correlation hole.

Exercise

Let us solve a Hooke's atom problem and compute the exchange-correlation hole. The system consists of two electrons confined in a Harmonic potential and the Hamiltonian is written as

$$\widehat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

which is a model He atom. Using the center of mass coordinate $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$ and the relative coordinate $\boldsymbol{u} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, the Hamiltonian becomes

$$\hat{H} = -\frac{1}{4}\nabla_{\boldsymbol{R}}^2 - \nabla_{\boldsymbol{u}}^2 + kR^2 + \frac{1}{4}ku^2 + \frac{1}{u},$$

so that the wave function can be decomposed into a product $\Psi(\mathbf{r}_1, \boldsymbol{r}_2) = \chi(\boldsymbol{R})\Phi(\boldsymbol{u})$ and the Schrödinger equation becomes

$$\left(-\frac{1}{4}\nabla_{\boldsymbol{R}}^2 + kR^2\right)\chi(\boldsymbol{R}) = E_{\boldsymbol{R}}\chi(\boldsymbol{R})$$

$$\left(-\nabla_{\boldsymbol{u}}^2 + \frac{1}{4}ku^2 + \frac{1}{u}\right)\Phi(\boldsymbol{u}) = E_{\boldsymbol{u}}\Phi(\boldsymbol{u}).$$

The first differential equation provides the well-known solution

$$\chi_{\boldsymbol{n}}(\boldsymbol{R}) = \frac{1}{\sqrt{2^{n_x n_y n_z} n_x!\, n_y!\, n_z!}}\left(\frac{2\sqrt{k}}{\pi}\right)^{\frac{3}{4}} e^{-\sqrt{k}R^2} H_{n_x}\left(2^{1/2}k^{1/4}R_x\right) H_{n_y}\left(2^{1/2}k^{1/4}R_y\right) H_{n_z}\left(2^{1/2}k^{1/4}R_z\right)$$

$$E_{\boldsymbol{R},\boldsymbol{n}} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\sqrt{k}$$

The second one is centrosymmetric and the solution should have a form

$$R_l(u)Y_{lm}(\bar{u})$$

and the equation for the radial part is

$$\left(-\frac{1}{u^2}\frac{d}{du}\left(u^2\frac{\partial}{du}\right) + \frac{l(l+1)}{u^2} + \frac{1}{4}ku^2 + \frac{1}{u}\right)R_l(u) = E_{\boldsymbol{u},l}R_l(u)$$

By rewriting $R_l(u)$

$$R_l(u) = \frac{e^{-\frac{\sqrt{k}}{4}u^2}T_l(u)}{u},$$

we obtain

$$\left(-\frac{d^2}{du^2} + \sqrt{k}u\frac{d}{du} + \frac{l(l+1)}{u^2} + \frac{\sqrt{k}}{2} + \frac{1}{u}\right)T_l(u) = E_{\boldsymbol{u},l}T_l(u).$$

Following the Frobenius method, let us express the regular solution for $T_l(u)$ as

$$T_l(u) = u^{l+1}\sum_{i=0}^{\infty} a_i u^i$$

and require that the recursion of the coefficient a_i

$$-(i+l+1)(i+l)a_i u^{i+l-1} + \sqrt{k}(i+l+1)a_i u^{i+l+1} + l(l+1)a_i u^{i+l-1} + \left(\frac{\sqrt{k}}{2} - E_{\boldsymbol{u},l}\right)a_i u^{i+l+1} + a_i u^{i+l} = 0$$

to terminate at some point of i. The recursion is rewritten as

$$\left[-(i+l+2)(i+l+1)a_{i+1} + \sqrt{k}(i+l)a_{i-1} + l(l+1)a_{i+1} + \left(\frac{\sqrt{k}}{2} - E_{\boldsymbol{u},l}\right)a_{i-1} + a_i\right]u^{i-1} = 0$$

so that

$$a_{i+1} = \frac{a_i + \left(\sqrt{k}\left(i + l + \frac{1}{2}\right) - E_{\boldsymbol{u},l}\right) a_{i-1}}{(i+1)(i+2l+2)}$$

$$a_1 = \frac{a_0}{2(l+1)}, a_2 = \frac{a_0}{2(2l+3)}\left(\frac{1}{2(l+1)} + \sqrt{k}\left(l + \frac{3}{2}\right) - E_{\boldsymbol{u},l}\right).$$

$$a_3 = \frac{a_2 + \left(\sqrt{k}\left(l + \frac{5}{2}\right) - E_{\boldsymbol{u},l}\right) a_1}{3(2l+4)}$$

The termination condition depends on the value of $\sqrt{k}$, and the simplest solution can be found for those parameters which vanish a_2 and a_3: The result is

$$\sqrt{k} = \frac{1}{2(l+1)}$$

and

$$E_{\boldsymbol{u},l} = \frac{2l+5}{4(l+1)}.$$

Namely, for the harmonic potential of strength $k = 4(l+1)^2$, analytical solution can be found. (Other solutions can be found by vanishing a with higher indices.)

The radial wave function is

$$R_l(u) = u^l\left(1 + \frac{1}{2(l+1)}u\right)e^{-\frac{u^2}{8(l+1)}}$$

and thus, the wave function for the relative coordinate is

$$\Phi(\boldsymbol{u}) = u^l\left(1 + \frac{1}{2(l+1)}u\right)e^{-\frac{u^2}{8(l+1)}}Y_{lm}(\overline{\boldsymbol{u}}).$$

When multiplied by the state with the lowest energy for the center of mass $\chi_{\boldsymbol{0}}(\boldsymbol{R})$ is

$$\begin{aligned}\chi_{\boldsymbol{0}}(\boldsymbol{R})\Phi(\boldsymbol{u}) &= \left(\frac{1}{\pi(l+1)}\right)^{\frac{3}{4}} e^{-\frac{R^2}{2(l+1)}}u^l\left(1 + \frac{1}{2(l+1)}u\right)e^{-\frac{u^2}{8(l+1)}}Y_{lm}(\overline{\boldsymbol{u}}) \\ &= \left(\frac{1}{\pi(l+1)}\right)^{\frac{3}{4}} e^{-\frac{(r_1^2+r_2^2)}{4(l+1)}}|\boldsymbol{r}_2 - \boldsymbol{r}_1|^l\left(1 + \frac{1}{2(l+1)}|\boldsymbol{r}_2 - \boldsymbol{r}_1|\right)Y_{lm}(\overline{\boldsymbol{r}_2 - \boldsymbol{r}_1}).\end{aligned}$$

After normalization,

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = N_l e^{-\frac{(r_1^2+r_2^2)}{4(l+1)}}|\boldsymbol{r}_2 - \boldsymbol{r}_1|^l\left(1 + \frac{1}{2(l+1)}|\boldsymbol{r}_2 - \boldsymbol{r}_1|\right)Y_{lm}(\overline{\boldsymbol{r}_2 - \boldsymbol{r}_1}).$$

Pair density is then obtained as

$$\begin{aligned}n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) &= N_l^2 e^{-\frac{(r_1^2+r_2^2)}{2(l+1)}}|\boldsymbol{r}_2 - \boldsymbol{r}_1|^{2l}\left(1 + \frac{1}{2(l+1)}|\boldsymbol{r}_2 - \boldsymbol{r}_1|\right)^2 \sum_{m=-l}^{l}|Y_{lm}(\overline{\boldsymbol{r}_2 - \boldsymbol{r}_1})|^2 \\ &= N_l^2\frac{2l+1}{4\pi}e^{-\frac{(r_1^2+r_2^2)}{2(l+1)}}|\boldsymbol{r}_2 - \boldsymbol{r}_1|^{2l}\left(1 + \frac{1}{2(l+1)}|\boldsymbol{r}_2 - \boldsymbol{r}_1|\right)^2\end{aligned}$$

after taking average over the degenerate states. The electron density is obtained as

$$2N_l^2 \iiint \frac{2l+1}{4\pi} e^{-\frac{(r_1^2+r^2)}{2(l+1)}} |\boldsymbol{r}-\boldsymbol{r}_1|^{2l} \left(1+\frac{1}{2(l+1)}|\boldsymbol{r}-\boldsymbol{r}_1|\right)^2 d\boldsymbol{r}_1$$

$$= 2N_l^2 \iiint \frac{2l+1}{4\pi} e^{-\frac{2r^2+u^2-2ru\cos\theta}{2(l+1)}} u^{2l} \left(1+\frac{1}{2(l+1)}u\right)^2 2\pi u^2 \sin\theta \, du d\theta.$$

Therefore,

$$n(\boldsymbol{r}) = 2N_0^2 \left(e^{-r^2} + e^{-\frac{r^2}{2}} \sqrt{\frac{\pi}{2}} \left(\frac{7}{4} + \frac{r^2}{4} + \left(r+\frac{1}{r}\right) \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right)\right)\right)$$

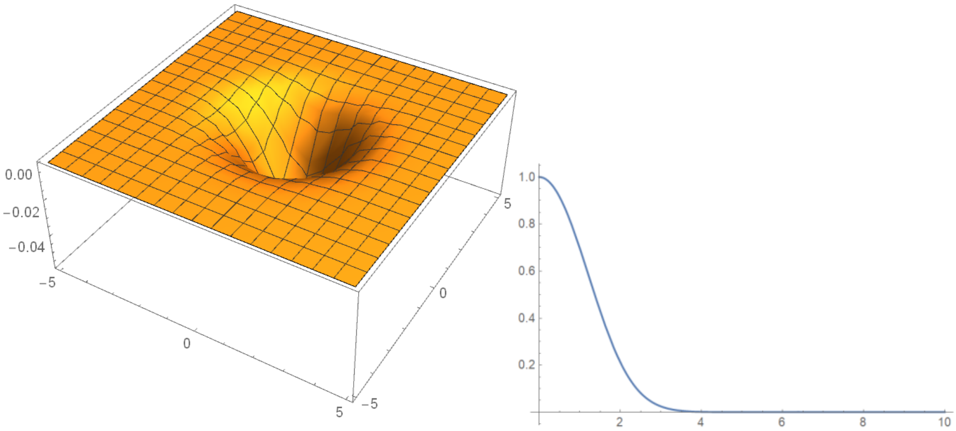
for $l = 0$ and

$$n(\boldsymbol{r}) = 2N_1^2 \left(6e^{-\frac{r^2}{2}}(10+r^2) + \frac{3\sqrt{\pi}e^{-\frac{r^2}{4}}(156r + 36r^3 + r^5 + 8(12 + 12r^2 + r^4) \operatorname{erf}\left(\frac{r}{2}\right)}{8r}\right)$$

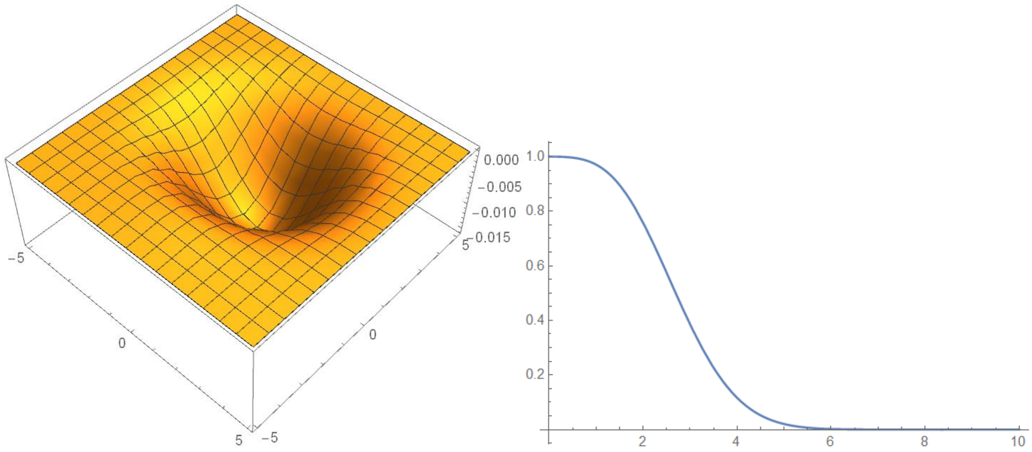
for $l = 1$. The exchange-correlation hole is then obtained from

$$n_{\mathrm{xc}}(\boldsymbol{r}_2; \boldsymbol{r}_1) = \frac{n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) - n(r_1)n(r_2)}{n(r_1)}.$$

For $l = 0$, it looks like



Here the first electron is located at $\boldsymbol{r}_1 = (1,0,0)$ and the coordinate of the second electron is taken as $\boldsymbol{r}_2 = (x, y, 0)$. The aim of KS-DFT is to establish the relationship between the electron density (right; unnormalized) and the (exchange-)correlation hole (left). For $l = 1$, the exchange-correlation hole looks like



$l = 1$ is an excited state, so that this is outside the scope of DFT strictly.

Returning to the main steam, let us continue the discussion on the exchange-correlation hole. We can separate the exchange-correlation functional into exchange and correlation. This can be done by using the pair density of the Kohn-Sham single-determinant $\Phi[n]$ as

$$n_{2,\mathrm{KS}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = n(\boldsymbol{r}_1)n(\boldsymbol{r}_2) + n(\boldsymbol{r}_1)n_{\mathrm{x}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$$

The exchange hole can be written using the Kohn-Sham orbitals as

$$n_{\mathrm{x}}(r_1, r_2)n(r_1) = -\sum_{\sigma}\left|\sum_{j}^{N}\phi_j^*(r_1\sigma)\phi_j(r_2\sigma)\right|^2,$$

so that it is negative everywhere.

In weakly correlation cases, the exchange hole is much larger in magnitude than the correlation hole in general. Therefore, the major task of DFT in those systems is to find an appropriate functional form for the exchange plus relatively small contribution from the correlation. In practice, finding the form for the correlation is much more difficult. Note that, when using the above form for the change, which is implicitly the functional of the electron density via the Kohn-Sham orbitals, one needs to try to find the correlation functional only; when, on the other hand, when using a local (and approximate) value, one usually tries to find the form for the exchange-correlation without separating it into pieces.

Adiabatic connection

Here I introduce the important technique called adiabatic connection, with which to redefine the exchange-correlation. In my view, this is extremely important in connecting DFT to formally rigorous many-body theories.

In this scheme, we introduce a continue path between the non-interacting KS system and the target system of interest while keeping the density constant. The density is kept equal to the exact one. The Hamiltonian changes in the path as

$$\hat{H}^{\lambda} = \hat{T} + \lambda \hat{W}_{\mathrm{ee}} + \hat{\mathrm{V}}^{\lambda}, \tag{2.18}$$

where $\hat{\mathrm{V}}^{\lambda}$ is the external local potential operator playing a role to keep the density constant. Note that the Hamiltonian is the Kohn-Sham one when λ is zero and is the physical one when it is 1. Along the line we have discussed, we can introduce the HK functional for each λ.

$$F^{\lambda}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle \tag{2.19}$$

This functional can be decomposed into

$$F^{\lambda}[n] = T_s[n] + E_{\mathrm{H}}^{\lambda}[n] + E_{\mathrm{xc}}^{\lambda}[n] \tag{2.20}$$

with

$$E_{\mathrm{H}}^{\lambda}[n] = \frac{1}{2} \iint \frac{n(\boldsymbol{r}_1) n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \lambda d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \lambda E_{\mathrm{H}}[n], \tag{2.21}$$

$$E_{\mathrm{x}}^{\lambda}[n] = \langle \Phi[n] | \lambda \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle - E_{\mathrm{H}}^{\lambda}[n] = \lambda E_{\mathrm{x}}[n] \tag{2.22}$$

$$E_{c}^{\lambda}[n] = \langle \Psi^{\lambda}[n] | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Psi^{\lambda}[n] \rangle - \langle \Phi[n] | \hat{T} + \lambda \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle. \tag{2.23}$$

The last equation can be used to derive

$$\frac{\partial E_{c}^{\lambda}[n]}{\partial \lambda} = \langle \Psi^{\lambda}[n] | \hat{W}_{\mathrm{ee}} | \Psi^{\lambda}[n] \rangle - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle. \tag{2.24}$$

Here the Hellmann Feynman theorem has been used. Then, we can derive

$$E_c[n] = \int_0^1 \langle \Psi^{\lambda}[n] | \hat{W}_{\mathrm{ee}} | \Psi^{\lambda}[n] \rangle d\lambda - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle. \tag{2.25}$$

Therefore, only the potential contribution appears in the formulation. We can further rewrite the correlation energy as

$$E_c[n] = \frac{1}{2} \int_0^1 d\lambda \iint \frac{n(\boldsymbol{r}_1) n_c^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{2.26}$$

or

$$E_c[n] = \frac{1}{2} \iint \frac{n(\boldsymbol{r}_1) \bar{n}_c^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{2.27}$$

where

$$\bar{n}_c^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \int_0^1 d\lambda n_c^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2).$$

This indicates that it is the parameter averaged correlation functional that needs to be related to the density in DFT. Later, I will show that this can be done using the fluctuation dissipation theorem.

It seems to me that it is more difficult to obtain $\Psi^{\lambda}[n]$ than to obtain $\Psi[n]$. If this is true, the adiabatic connection has only conceptual importance.

Fractional number of electron

With DFT, it is plausible if one can consider the system under finite temperatures, where the system contains thermally excited state and thus the theory is no more a ground-state one. It is also plausible if one can study a subsystem interacting with host materials, and in addition, exchanging electrons with the host. Extension of DFT in those directions were discussed in the past. I will briefly explain the density functional theory for fractional number of electrons as a step towards those problems.

Let us denote the number as $\mathcal{N}$ which is also written as $\mathcal{N} = N - 1 + f$ with $N \in \mathbb{I}$ and $0 \leq f \leq 1$. The total-energy is described as

$$E_0^{\mathcal{N}} = \min_{\hat{\Gamma}} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \widehat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}\right)\right], \tag{2.30}$$

using the ensemble density matrix defined as

$$\hat{\Gamma} = (1-f)|\Psi^{N-1}\rangle\langle\Psi^{N-1}| + f|\Psi^{N}\rangle\langle\Psi^{N}|. \tag{2.31}$$

(One may use many states with different number of electrons as well.) The variation is done for Ψ^{N-1} and Ψ^{N}, by which the ensemble density matrix is obtained as

$$\hat{\Gamma}_0 = (1-f)|\Psi_0^{N-1}\rangle\langle\Psi_0^{N-1}| + f|\Psi_0^{N}\rangle\langle\Psi_0^{N}|. \tag{2.32}$$

Then the total-energy can be described as

$$E_0^{\mathcal{N}} = (1-f)E_0^{N-1} + fE_0^{N}.$$

From this definition, it is clear that the total-energy has a derivative discontinuity as

$$\frac{dE_0^{\mathcal{N}}}{d\mathcal{N}} = \begin{cases} E_0^{N} - E_0^{N-1} \equiv -I_N \text{ when } N-1 < \mathcal{N} < N \\ E_0^{N+1} - E_0^{N} \equiv -A_N \text{ when } N < \mathcal{N} < N+1 \end{cases}$$

Usually, the ionization I_N and the affinity A_N are different, so that the electronic chemical potential $dE_0^{\mathcal{N}}/d\mathcal{N} \equiv \mu$ is discontinuous at the integer number: This is called integer discontinuity. Note that the fundamental gaps, or the HOMO-LUMO gap, is defined as

$$I_N - A_N \equiv E_{\mathrm{gap}}^{N}.$$

DFT for fractional number of electrons assumes existence of universal HK functional

$$F[n] = \min_{\hat{\Gamma}\to n} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \widehat{W}_{\mathrm{ee}}\right)\right]. \tag{2.38}$$

This can be decomposed, in the KS theory, into

$$F[n] = T_s[n] + E_{\mathrm{Hxc}}[n] \tag{2.39}$$

where the Kohn-Sham non-interacting kinetic energy is given as

$$T_s[n] = \min_{\hat{\Gamma}_s \to n} \mathrm{Tr}[\hat{\Gamma}_s \hat{T}],$$

and the ensemble non-interacting density matrix is

$$\hat{\Gamma}_s = (1-f)\,|\Phi^{N-1,f}\rangle\langle\Phi^{N-1,f}| + f|\Phi^{N,f}\rangle\langle\Phi^{N,f}|. \tag{2.41}$$

The total-energy can also be described using the Kohn-Sham orbitals in a way very similar to the one shown above, but here I show the resulting equations. By introducing partial occupation number of each KS orbitals n_i, the total-energy can be described as

$$E = \sum_i^N n_i \int \phi_i^*(\boldsymbol{r})\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r})d\boldsymbol{r} + E_{\mathrm{Hxc}}[n], \tag{2.42}$$

with the density

$$n(\boldsymbol{r}) = \sum_i^N n_i|\phi_i(\boldsymbol{r})|^2. \tag{2.43}$$

Note that the occupation number satisfy the condition that $n_i = 1$ for $i \leq N-1$ and $n_N = f$. The KS equation is thereby unchanged

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}) \tag{2.44}$$

$$v_{\mathrm{s}}(\boldsymbol{r}) = v_{\mathrm{ne}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r})}. \tag{2.45}$$

It should be reminded, however, the derivative with respect to the electron density becomes ambiguous when allowing change in the number of electrons. Therefore $\delta E_{\mathrm{Hxc}}[n]$ should be understood in terms of

$$\delta E_{\mathrm{Hxc}}[n] = \int \left(\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r})} + \mathrm{const}\right)\delta n(\boldsymbol{r})d\boldsymbol{r} \tag{2.46}$$

and the change in the number of electrons should be carefully taken into account to determine the constant, as will be shown in the next subsection. From the above equations, we can derive

$$\frac{\partial E}{\partial n_i} = \varepsilon_i. \tag{2.46}$$

This is called Janak theorem. Recall the Koopmans theorem of the Hartree-Fock, which is similar to Eq. (2.46) but is different in that the differentiation is replaced by finite difference in the Koopmans.

LUMO energy and the derivative discontinuity

From the Janak theorem, the derivative at a number slightly larger than an integer is,

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}\right)_{N+\delta} = \varepsilon_{\mathrm{HOMO}}^{N+\delta}, \tag{2.54}$$

where the right-hand side is equal to the HOMO energy at $N+1$-th orbital. Since Eq. (2.54) is identical to the definition of the affinity, we have

$$\varepsilon_{\mathrm{HOMO}}^{N+\delta} = -A_N. \tag{2.55}$$

This means that the affinity can be calculated using the HOMO energy. But, actually, this is unrelated to the LUMO energy. To see it, let us write the HOMO orbital in terms of the KS orbitals as

$$\varepsilon_{\mathrm{HOMO}}^{N+\delta} = \int \phi_{\mathrm{HOMO}}^{N+\delta}(\boldsymbol{r})^* \left(-\frac{1}{2}\nabla^2 + v_s^{N+\delta}(\boldsymbol{r})\right) \phi_{\mathrm{HOMO}}^{N+\delta}(\boldsymbol{r}) d\boldsymbol{r}. \tag{2.56}$$

The naive counterpart will be the LUMO energy of a system with a number slightly smaller than N. The corresponding LUMO energy is

$$\varepsilon_{\mathrm{LUMO}}^{N-\delta} = \int \phi_{\mathrm{LUMO}}^{N-\delta}(\boldsymbol{r})^* \left(-\frac{1}{2}\nabla^2 + v_s^{N-\delta}(\boldsymbol{r})\right) \phi_{\mathrm{LUMO}}^{N-\delta}(\boldsymbol{r}) d\boldsymbol{r}. \tag{2.57}$$

With decreasing $\delta \to 0^+$, $v_s^{N+\delta}(\boldsymbol{r})$ and $v_s^{N-\delta}(\boldsymbol{r})$ approach the potentials that are equal to each other except for the additive constant, $v_s^{N+\delta}(\boldsymbol{r}) - v_s^{N-\delta}(\boldsymbol{r}) \equiv \Delta_{\mathrm{xc}}^N$. Therefore,

$$\varepsilon_{\mathrm{HOMO}}^{N+\delta} = \varepsilon_{\mathrm{LUMO}}^{N-\delta} + \Delta_{\mathrm{xc}}^N \tag{2.58}$$

holds. Namely, after taking the limit,

$$\varepsilon_{\mathrm{LUMO}}^{N} = -A_N - \Delta_{\mathrm{xc}}^N. \tag{2.60}$$

This allows to rewrite the fundamental gap in terms of the derivative discontinuity as

$$E_{\mathrm{gap}}^N = \varepsilon_{\mathrm{LUMO}}^N - \varepsilon_{\mathrm{HOMO}}^N + \Delta_{\mathrm{xc}}^N. \tag{2.63}$$

The constant appeared in the derivation of HK theorem turns out to be the derivative discontinuity.

Existing approximate functionals

There are many different functionals of different level of approximations. Usually, there is a trend that the more complex the functional is the more accurate the result is, but this does not mean superiority in all respects. A functional can be more accurate in one respect but is less accurate in the other respects. Let us briefly survey popular functionals.

Local density approximation (LDA): The exchange-correlation of LDA can be written as

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(r)\varepsilon_{\mathrm{xc}}^{\text{uniform gas}}(n(\boldsymbol{r}))d\boldsymbol{r}.$$

ε is obtained by doing a Monte Carlo simulation of uniform electron gas of a fixed electron density. The result of the exchange-correlation energy is fitted to a form

$$-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}(\boldsymbol{r}) + \varepsilon_c(r_s(n(\boldsymbol{r})))$$

$$\varepsilon_c(r_s) = \begin{cases} A\ln r_s + B + C\, r_s \ln r_s & \text{when } r_s \le r_{s,0} \\ \dfrac{a}{r_s} + \dfrac{b}{r_s^{3/2}} & \text{when } r_s > r_{s,0} \end{cases}$$

where $r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$.

Generalized gradient approximation (GGA): LDA is based on the uniform electron gas and therefore is more accurate for a system having more uniform electron density. This means LDA favors too much metallic systems over insulating systems and favors also condensed phases over isolated phases like an atom. This is a serious drawback when comparing phases of different electronic structure. It is also known that the adsorption energy on the surface or atomization energy is too large and is beyond the required chemical accuracy. As a method to overcome it, gradient of the electron density is incorporated into the functional. A natural form for the gradient corrected exchange-correlation functional is obtained by expanding by the dimensionless parameter $\nabla n(\boldsymbol{r})/n(\boldsymbol{r})^{4/3}$ as

$$E_{\mathrm{xc}}^{\mathrm{GEA}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] + \int C_{\mathrm{xc}}\big(n(\boldsymbol{r})\big)n(\boldsymbol{r})^{\frac{4}{3}}\left(\frac{\nabla n(\boldsymbol{r})}{n(\boldsymbol{r})^{\frac{4}{3}}}\right)^2 d\boldsymbol{r}, \tag{3.10}$$

The expansion parameter, however, can be large in some part of the target system making the expansion break down. In this context, people have tried to construct a functional so that

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int f\big(n(\boldsymbol{r}), \nabla n(\boldsymbol{r})\big) d\boldsymbol{r} \tag{3.11}$$

Note that LDA uses a local approximation to the exchange-correlation, in this sense GGA is said to be a semi-local approximation scheme for the exchange-correlation. Some works nicely at crystalline phases and others at surfaces, and so on. For details, please read the textbooks shown at the beginning.

GGA[#1] B88 exchange functional: Becke 88 was constructed to reproduce the nonlocal exchange functional (Eq. (1.26)), such as the asymptotic behavior of the exchange energy per particle and the value of the nonlocal exchange energy of rare-gas atoms.

GGA[#2] LYP correlation functional: Lee-Yang-Parr (LYP) correlation functional was constructed based on an approximation of the Hartree-Fock pair density.

GGA[#3] PW91 exchange-correlation functional: Perdew-Wang 91 exchange-correlation functional is based on a model of the exchange hole (Eq. (2.14)) and the coupling-constant-averaged correlation hole (Eq. (2.29)).

GGA[#4] PBE exchange-correlation functional: Perdew-Burke-Ernzerhof exchange-correlation functional is a simplified PW91.

Meta GGA: Meta GGA is based on the description of the functional using the second derivative of the density and the newly introduced quantity $\tau(\boldsymbol{r})$ defined by Eq. (3.14).

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int f\big(n(\boldsymbol{r}), \nabla n(\boldsymbol{r}), \nabla^2 n(\boldsymbol{r}), \tau(\boldsymbol{r})\big) d\boldsymbol{r} \tag{3.13}$$

$$\tau(\boldsymbol{r}) = \frac{1}{2}\sum_{i}^{N} |\nabla \phi_i(\boldsymbol{r})|^2 \tag{3.14}$$

$\tau(\boldsymbol{r})$ is constructed by the square of the KS gradient. This quantity is distinct from the electron density and thus the ground-state energy is given formally as

$$E_0 = \min_{\Phi}\langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{H}}[n_\Phi] + E_{\mathrm{xc}}[n_\Phi, \tau_\Phi].$$

Therefore, it is a slight extension of the KS-DFT formalism. Meta GGA is generally superior to GGA but requires dedicated basis functions or finer real-space mesh.

Hybrid DFT: Becke proposed to mix the nonlocal exchange energy, or the Hartree-Fock exchange energy,

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma}\sum_{ij}^{N_\sigma} \iint \frac{\phi_{i\sigma}^*(\boldsymbol{r}_1)\phi_{j\sigma}(\boldsymbol{r}_1)\phi_{j\sigma}^*(\boldsymbol{r}_2)\phi_{i\sigma}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2, \tag{3.18}$$

with the existing forms for the exchange and correlation, such as

$$E_{\mathrm{xc}}^{\mathrm{3H}} = aE_{\mathrm{x}}^{\mathrm{HF}} + bE_{x}^{\mathrm{GGA}} + (1-a-b)E_{x}^{\mathrm{LDA}} + cE_{\mathrm{c}}^{\mathrm{GGA}} + (1-c)E_{\mathrm{c}}^{\mathrm{LDA}}. \tag{3.17}$$

The most famous parameterization is known as B3LYP, which was constructed by using the B88 exchange for the GGA exchange and the LYP correlation for the GGA correlation. Another form is

$$E_{\mathrm{xc}}^{\mathrm{1H}} = aE_{\mathrm{x}}^{HF} + (1-a)E_{\mathrm{x}}^{\mathrm{DFA}} + E_{\mathrm{c}}^{\mathrm{DFA}}, \tag{3.19}$$

where DFA stands for any semilocal density functional approximation (DFA). The most famous one is called PBE0 where the fitting parameter was set to be 0.25. Hybrid DFT is rather free from the self-interaction error. The mixing parameters, a to c, are determined by comparing with the experimental data for selected matters: Because of its highly empirical nature, the range of applicability should be limited. It is also noted that hybrid DFT generally works for insulators but sometimes fails for metals.

Double hybrid DFT: Grimme constructed

$$E_{\mathrm{xc}}^{\mathrm{2DH}} = a_{\mathrm{x}}E_{\mathrm{x}}^{HF} + (1-a_{\mathrm{x}})E_{\mathrm{x}}^{\mathrm{DFA}} + (1-a_{\mathrm{c}})E_{\mathrm{c}}^{\mathrm{DFA}} + a_{\mathrm{c}}E_{\mathrm{c}}^{\mathrm{MP2}}, \tag{3.22}$$

where MP2 stands for the second order approximation to the correlation energy

$$E_{\mathrm{c}}^{\mathrm{MP2}} = -\frac{1}{4}\sum_{ij=1}^{N}\sum_{ab=N+1}^{2M}\frac{\left|\langle\psi_i\psi_j|\psi_a\psi_b\rangle - \langle\psi_i\psi_j|\psi_b\psi_a\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \tag{3.23}$$

where the bracket appearing in the numerator indicates the Coulomb integral

$$\langle\psi_i\psi_j|\psi_a\psi_b\rangle = \iint \frac{\psi_i^*(\boldsymbol{r}_1)\psi_j^*(\boldsymbol{r}_2)\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{x}_1 d\boldsymbol{x}_2. \tag{3.24}$$

Note that a and b is large than N indicating that unoccupied KS orbitals are included in the formalism contrary to others introduced so far, where only occupied orbitals are included. This way, the computation of the functional are becoming more and more demanding although the accuracy is generally improving by that.

Range-separated hybrid DFT: Iikura, Tsuneda, Yanai, and Hirao proposed a long-range correction (LC) scheme to assign different forms for the exchange depending on the distance between the electrons as

$$E_{\mathrm{xc}}^{\mathrm{LC}} = E_{\mathrm{x}}^{\text{long range,HF}} + E_{\mathrm{x}}^{\text{short range,DFA}} + E_{\mathrm{c}}^{\mathrm{DFA}}.$$

The range-separation is done using the error function as

$$E_{\mathrm{x}}^{\text{long range,HF}} = -\frac{1}{2}\sum_{\sigma}\sum_{ij}^{N_\sigma}\iint \frac{\phi_{i\sigma}^*(\boldsymbol{r}_1)\phi_{j\sigma}(\boldsymbol{r}_1)\mathrm{erf}(\mu|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\phi_{j\sigma}^*(\boldsymbol{r}_2)\phi_{i\sigma}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2, \tag{3.27}$$

This is based on the idea that the error of the semilocal approximation to the exchange is serious when two electrons are apart and the error is effectively corrected by the HF exchange. The cutoff distance for the range-separation needs to be introduced empirically.

Exact exchange (HF exchange)

In this scheme, the one-electron orbitals $\phi_{i\sigma}$ appearing in Eq. (3.18) is not treated as an independent variable but is regarded as a functional of the electron density $n(\boldsymbol{r})$. That is, the orbitals are treated as the solution of a KS equation where a (semi-)local form is used for the exchange-correlation functional. The exchange potential thereby generated is the derivative of Eq. (3.18),

$$\frac{\delta E_{\mathrm{x}}}{\delta v_s(\boldsymbol{r})} = \int \frac{\delta E_{\mathrm{x}}}{\delta n(\boldsymbol{r}')}\frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} d\boldsymbol{r}'. \tag{4.2}$$

The derivative of the electron density can be obtained by using the definition of the response function

$$\chi_0(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})}$$

as

$$\int v_{\mathrm{x}}(\boldsymbol{r}')\chi_0(\boldsymbol{r}',\boldsymbol{r})d\boldsymbol{r}' = \frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\mathbf{r})}. \tag{4.3}$$

That is, using the response function, change in the electron density with respect to the effective potential is expressed using the KS orbital as

$$\chi_0(\boldsymbol{r}',\boldsymbol{r}) = -\sum_{\sigma}\sum_{i=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}\iint \frac{\phi_{i\sigma}^*(\boldsymbol{r}')\phi_{a\sigma}(\boldsymbol{r})\phi_{a\sigma}^*(\boldsymbol{r})\phi_{i\sigma}(\boldsymbol{r}')}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}}d\boldsymbol{r}_1 d\boldsymbol{r}_2 + \mathrm{c.c.} \tag{4.5}$$

When this is used, we can derive the exchange potential using the two-electron integral as

$$\frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\boldsymbol{r})} = \sum_{\sigma}\sum_{ij=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}(\phi_{a\sigma}\phi_{j\sigma}|\phi_{j\sigma}\phi_{i\sigma})\frac{\phi_{a\sigma}(\boldsymbol{r})\phi_{i\sigma}^*(\boldsymbol{r})}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}} + \mathrm{c.c.} \tag{4.6}$$

This method for expressing the HF exchange is called optimized effective potential (OEP) method.

Second-order Görling-Levy perturbation theory

The Hamiltonian appearing in the adiabatic connection, $\hat{H}^\lambda = \hat{T} + \lambda\hat{W}_{\mathrm{ee}} + \hat{\mathrm{V}}^\lambda$, is decomposed using $\hat{\mathrm{V}}^\lambda = \hat{V}_{\mathrm{s}} - \lambda\hat{V}_{\mathrm{Hx}} - \hat{V}_{\mathrm{c}}^\lambda$ as

$$\hat{H}^\lambda = (\hat{T} + \hat{V}_{\mathrm{s}}) + \lambda(\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}) - \hat{V}_{\mathrm{c}}^\lambda,$$

following the second order expansion of $\hat{V}_{\mathrm{c}}^\lambda$ with respect to λ, which starts from the second order as $\hat{V}_{\mathrm{c}}^\lambda = \lambda^2\hat{V}_{\mathrm{c}}^{(2)}$. Then the perturbation theory is applied to the KS state $\Phi_{n=0}$ as

$$|\Psi^{(1)}\rangle = -\sum_{n\neq 0}|\Phi_n\rangle\frac{\langle\Phi_n|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Phi_n\rangle}{\mathcal{E}_n - \mathcal{E}_0},$$

and this expression is inserted into Eq. (2.23)

$$E_{\mathrm{c}}^\lambda = \langle\Psi^\lambda|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi^\lambda\rangle - \langle\Phi|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Phi\rangle$$

to obtain the correlation energy by expanding it in powers of λ. The result is

$$E_{\mathrm{c}}^{(2)} = \langle\Phi|\hat{W}_{\mathrm{ee}}|\Psi^{(1)}\rangle = \langle\Phi|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Psi^{(1)}\rangle = -\sum_{n\neq 0}|\frac{|\langle\Phi|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Phi_n\rangle|^2}{\mathcal{E}_n - \mathcal{E}_0}.$$

It was found this does not improve the correlation satisfactorily, indicating that it is necessary to go beyond the second order approximation.

There are so many types of approximation. As we have seen above, some of them are introduced to approximate the HF exchange, which takes large computational time, with semi local one, for which the computational time is generally much smaller. Others are introduced to better describe the correlation functionals semilocally. In many cases, the accuracy has been improved empirically in the sense that fitting parameters are introduced to better reproduce experiments or accurate simulations. This idea is recently combined with machine learning methods which enable to use much flexible fitting functions like neural network. Contrary to this approach, there have been trials to derive plausible functionals theoretically.

Fluctuation dissipation formula

To derive the functional form theoretically, I will introduce the general idea of many-body theories called fluctuation dissipation formula that relates the correlation described using the pair density $n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ with the fluctuation $\langle\Psi|\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)|\Psi\rangle$ described by the expectation value of the pair density operator. The fluctuation is known to be more easily evaluated than the correlation when the fluctuation is described by using the response functions. Note that this is a step toward combining the density functional theory with the many-body theory.

Density operator

To compactly describe the fluctuation dissipation theorem, let us introduce the density operator without using the terminology of the field theory. The density operator is defined as

$$\hat{n}_1(\boldsymbol{r}) = \sum_i^N \delta(\boldsymbol{r}-\boldsymbol{r}_i)$$

where $\boldsymbol{r}_i$ is the coordinate of the constituent N electrons and $\boldsymbol{r}$ is a point in real-space. The density can be obtained as

$$n(\boldsymbol{r}) = \langle\Psi|\hat{n}_1(\boldsymbol{r})|\Psi\rangle.$$

The pair density operator can also be defined as

$$\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2) - \hat{n}_1(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1-\boldsymbol{r}_2).$$

Those are used to obtain

$$\hat{T} = -\frac{1}{2}\int [\nabla_{\boldsymbol{r}}^2 \hat{n}_1(\boldsymbol{r},\boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}} d\boldsymbol{r}$$

$$\widehat{W}_{\mathrm{ee}} = \frac{1}{2}\iint w_{\mathrm{ee}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\hat{V}_{\mathrm{ne}} = \int v_{\mathrm{ne}}(\boldsymbol{r})\hat{n}(\boldsymbol{r})d\boldsymbol{r}$$

To obtain the correlation energy using the adiabatic connection,

$$E_{\mathrm{c}} = \int_0^1 d\lambda \left\langle\Psi^\lambda\middle|\widehat{W}_{\mathrm{ee}}\middle|\Psi^\lambda\right\rangle - \left\langle\Phi\middle|\widehat{W}_{\mathrm{ee}}\middle|\Phi\right\rangle = \frac{1}{2}\int_0^1 d\lambda \iint \frac{n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2, \qquad (4.15)$$

we need the quantity

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2) = n_2^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2) - n_{2,\mathrm{KS}}(\boldsymbol{r}_1,\boldsymbol{r}_2).$$

Using the relations

$$n_2^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2) = \langle\Psi^\lambda|\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)|\Psi^\lambda\rangle = \langle\Psi^\lambda|\hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2)|\Psi^\lambda\rangle - \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\langle\Psi^\lambda|\hat{n}_1(\boldsymbol{r}_1)|\Psi^\lambda\rangle$$

$$n_{2,\mathrm{KS}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \langle\Phi|\hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2)|\Phi\rangle - \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\langle\Phi|\hat{n}_1(\boldsymbol{r}_1)|\Phi\rangle \qquad (4.16-4.17)$$

and the fact that the density is independent of λ, we have

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2) = \langle\Psi^\lambda|\hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2)|\Psi^\lambda\rangle - \langle\Phi|\hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2)|\Phi\rangle. \qquad (4.18)$$

Now we relate the correlation function to the response function, i.e. response of the density to the external perturbation. Equation (4.5) is a static response function

$$\chi_0(\boldsymbol{r}',\boldsymbol{r}) = \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})}$$

but it is better to use a time-dependent one like

$$\chi_0(\boldsymbol{r}'t',\boldsymbol{r}t) = \frac{\delta n(\boldsymbol{r}'t')}{\delta v_s(\boldsymbol{r}t)}.$$

We also need to consider that eq. (4.5) describes a response of the non-interacting system, but we need response of the interacting systems

$$\chi(\boldsymbol{r}'t',\boldsymbol{r}t) = \frac{\delta n(\boldsymbol{r}'t')}{\delta v_{\mathrm{ne}}(\boldsymbol{r}t)}.$$

For this purpose, we use a many-body Green's function formalism for the time-dependent Schrödinger equation. So, let us introduce the many-body Green's function formalism for a while and then return to the discussion on the fluctuation dissipation theorem.

Many-body Green's function (article 2)

We briefly introduce the many-body Green's function following another article written by Toulouse. For this purpose, we first change the language to that of the field theory. The Hamiltonian can be rewritten as

$$\hat{H} = \int d\boldsymbol{x}\,\hat{\psi}^\dagger(\boldsymbol{x})\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r})\right)\hat{\psi}(x) + \frac{1}{2}\iint d\boldsymbol{x}_1 d\boldsymbol{x}_2\,\hat{\psi}^\dagger(\boldsymbol{x}_1)\hat{\psi}^\dagger(\boldsymbol{x}_2)v(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{\psi}(\boldsymbol{x}_2)\hat{\psi}(\boldsymbol{x}_1),$$

where $v(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the Coulombic interaction $1/|\boldsymbol{r}_1-\boldsymbol{r}_2|$ and the term parenthesized in the first term $-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r})$ will be denoted as $h(\boldsymbol{r})$. Here we have introduced the field operator

$$\psi(\boldsymbol{x}) \equiv \sum_{\mathrm{i}} \psi_i(\boldsymbol{x})\hat{c}_i,$$

which will be time-evolved using the Heisenberg representation as

$$\psi(1) \equiv \psi(\boldsymbol{x}_1,t_1) = e^{i\hat{H}t_1}\psi(\boldsymbol{x}_1)e^{-i\hat{H}t_1}.$$

This is just a rewrite of equations but helps to make equations much simpler. I intuitively note that the "physical" Green's function is the retarded one but "convenient" Green's function is the time-ordered one; there is a way to make the former from the latter. The time-ordered Green's function is given for an N electron system by

$$\begin{aligned} \mathrm{i}G(1{,}2) &= \langle N|T[\hat{\psi}(1)\hat{\psi}^{\dagger}(2)]|N\rangle \\ &= \begin{cases} \langle N|\hat{\psi}(1)\hat{\psi}^{\dagger}(2)|N\rangle & \text{when } \mathrm{t}_1 > t_2 \\ -\langle N|\hat{\psi}^{\dagger}(2)\hat{\psi}(1)|N\rangle & \text{when } \mathrm{t}_1 < t_2 \end{cases} \end{aligned} \tag{2}$$

Here operators are ordered from the more past ones to the more recent ones. The Green's function follows the equation of motion

$$\left(\mathrm{i}\frac{\partial}{\partial t} + \frac{\nabla^2}{2}\right)G(1{,}2) = \delta(1-2) - i\sum_{\sigma_3} v(3{,}1)\,\langle N|T[\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^{\dagger}(2)]|N\rangle.$$

This can be derived as follows:

First, consider the equation of motion of the field operator, which is

$$\frac{\partial\hat{\psi}(1)}{\partial t_1} = -\mathrm{i}e^{\mathrm{i}\hat{H}t_1}[\hat{\psi}(\boldsymbol{x}_1),\hat{H}]e^{-\mathrm{i}\hat{H}t_1}.$$

By calculating the commutation relation, we get

$$[\hat{\psi}(\boldsymbol{x}_1),\hat{H}] = h(\boldsymbol{r}_1)\hat{\psi}(\boldsymbol{x}_1) + \int d\boldsymbol{x}_2\,\hat{\psi}^{\dagger}(\boldsymbol{x}_2)v(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{\psi}(\boldsymbol{x}_2)\psi(\boldsymbol{x}_1)$$

and then

$$\frac{\partial\hat{\psi}(1)}{\partial t_1} = -\mathrm{i}h(1)\hat{\psi}(1) - i\int d3\hat{\psi}(3)v(1{,}3)\hat{\psi}(3)\hat{\psi}(1).$$

This can be used time derivative of the one-body Green's function

$$\begin{aligned} \mathrm{i}\frac{\partial}{\partial t_1}G(1{,}2) &= \delta(t_1-t_2)\langle N|\hat{\psi}(1)\hat{\psi}^{\dagger}(2)|N\rangle + \theta(t_1-t_2)\left\langle N\middle|\frac{\partial\hat{\psi}(1)}{\partial t_1}\hat{\psi}^{\dagger}(2)\middle|N\right\rangle \\ &\quad - \delta(t_1-t_2)\langle N|\hat{\psi}^{\dagger}(2)\hat{\psi}(1)|N\rangle - \theta(t_1-t_2)\left\langle N\middle|\hat{\psi}^{\dagger}(2)\frac{\partial\hat{\psi}(1)}{\partial t_1}\middle|N\right\rangle \end{aligned}$$

This can be simplified as

$$\begin{aligned} \mathrm{i}\frac{\partial}{\partial t_1}G(1{,}2) &= \delta(1{,}2) + h(1)G(1{,}2) \\ &\quad - i\int d3\,v(1{,}3)[\theta(t_1-t_2)\langle N|\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^{\dagger}(2)|N\rangle - \theta(t_2 \\ &\quad - t_1)\,\langle N|\hat{\psi}^{\dagger}(2)\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)|N\rangle \end{aligned}$$

Using the definition of the two-body Green's function as will appear below

$$\mathrm{i}^2G_2(1{,}2;1',2') = \langle N|T[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^{\dagger}(1')\hat{\psi}^{\dagger}(2')]|N\rangle,$$

further simplification is possible and the result is

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1{,}2) = \delta(1{,}2) + h(1)G(1{,}2) + \mathrm{i}\int d3v(1{,}3)G_2(1{,}3^{+};2{,}3^{++}),$$

where time is ordered as $t_3^{++} > t_3^{+} > t_3$ and the difference in the time is infinitesimal.

The one-body density matrix can be written as

$$n_1(\boldsymbol{x}_1,\boldsymbol{x}_2) = \langle N|\hat{\psi}^{\dagger}(\boldsymbol{x}_2)\hat{\psi}(\boldsymbol{x}_1)|N\rangle = -\mathrm{i}G(\boldsymbol{x}_1t_1,\boldsymbol{x}_2t_1^{+}). \tag{3}$$

and the one-body electron density as

$$n_1(\boldsymbol{x}_1,\boldsymbol{x}_2)=-\mathrm{i}\sum_\sigma G(\boldsymbol{r}_1\sigma t_1,\boldsymbol{r}_2\sigma t_1^+). \tag{4}$$

The Green's function can be rewritten using the completeness relation of $N\pm 1$ body states as

$$\mathrm{i}G(\boldsymbol{x}_1,\boldsymbol{x}_2,\tau)=\theta(\tau)\sum_a\langle N|\hat{\psi}(\boldsymbol{x}_1)|N+1,a\rangle\langle N+1,a|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N\rangle e^{-\mathrm{i}(E_{N+1,a}-E_N)\tau}$$
$$-\theta(-\tau)\sum_a\langle N|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N-1,a\rangle\langle N-1,a|\hat{\psi}(\boldsymbol{x}_1)|N\rangle e^{-\mathrm{i}(E_N-E_{N-1,a})\tau}, \tag{5}$$

so that the Fourier component is

$$G(\boldsymbol{x}_1,\boldsymbol{x}_2,\omega)=\sum_a\frac{\langle N|\hat{\psi}(\boldsymbol{x}_1)|N+1,a\rangle\langle N+1,a|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N\rangle}{\omega-E_{N+1,a}+E_N+i0^+}$$
$$+\sum_a\frac{\langle N|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N-1,a\rangle\langle N-1,a|\hat{\psi}(\boldsymbol{x}_1)|N\rangle}{\omega-E_{N-1,a}+E_N-i0^+}.$$

This is called the Lehman representation of the one-particle Green's function. It is simply rewritten as

$$=\sum_a\frac{f_a(\boldsymbol{x}_1)f_a^*(\boldsymbol{x}_2)}{\omega+A_a+i0^+}+\sum_i\frac{f_i(\boldsymbol{x}_1)f_i^*(\boldsymbol{x}_2)}{\omega-I_i-i0^+}, \tag{6}$$

where the affinity and ionization potential has been used. The function f appearing in the denominator is called as the (quasi particle) wave function.

Linear response and response function

At this moment, let us definite the linear-response function. For this, we will consider a system applied with a perturbation like

$$\hat{H}'(\mathrm{t})=\int\hat{n}(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r},t)d\boldsymbol{r}$$

and evaluate the expectation value of the density. We can use the equation of motion for the time-evolution operator in the interaction representation

$$\mathrm{i}\frac{\partial U_I(t,t_0)}{\partial t}=\hat{H}'_I(t)U_I(t,t_0)$$

which is solved as

$$U_I(t,t_0)\simeq 1-\mathrm{i}\int_{\mathrm{t}_0}^{\mathrm{t}}dt'\,\hat{H}'_I(t')=1-\mathrm{i}\int_{\mathrm{t}_0}^{\mathrm{t}}dt'\,e^{\mathrm{i}\hat{H}_0t'}\hat{H}(t')e^{-\mathrm{i}\hat{H}_0t'}.$$

Therefore, the expectation value of the density is given as

$$\delta n(\boldsymbol{r}t)=\langle U_I^\dagger(t,t_0)\hat{n}_I(\boldsymbol{r}t)U_I(t,t_0)\rangle.$$

The terms linear with respect to the perturbation is

$$\delta n(\boldsymbol{r}t) = i\int_{t_0}^{t} dt'^{\int dr'} \langle [\hat{n}_I(\boldsymbol{r}t), \hat{n}_I(\boldsymbol{r}'t')]\rangle V_{\text{ext}}(\boldsymbol{r}', t')$$

The response function is thus given by the density-density correlation function as

$$\chi(\boldsymbol{r}t, \boldsymbol{r}'t') = \mathrm{i}\langle [\hat{n}_I(\boldsymbol{r}t), \hat{n}_I(\boldsymbol{r}'t')]\rangle.$$

Here the subscript I may be regarded as the Heisenberg representation. Depending on the boundary condition, we can make the causal or time-ordered response function. Note that this is a plausible extension of the static definition $\hat{n}_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2) - \hat{n}_1(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$

One can likewise introduce the two-body Green's function as

$$\mathrm{i}^2 G_2(1,2;1',2') = \langle N | T[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2')] | N\rangle, \tag{7}$$

which describes the propagation of a pair of particles; electrons, holes, or electron-hole. A related quantity called four-point linear response function is defined as

$$\mathrm{i}\chi(1,2;1',2') = \mathrm{i}^2 G_2(1,2;1',2') - iG(1,1')iG(2,2'). \tag{8}$$

For a special time-ordering relation, it can be rewritten as

$$\begin{aligned} \mathrm{i}\chi(1,2;\boldsymbol{x}'_1 t_1^+, \boldsymbol{x}'_2 t_2^+) \\ &= \langle N | T[\hat{\psi}^\dagger(1')\hat{\psi}(1)\hat{\psi}^\dagger(2')\hat{\psi}(2)] | N\rangle \\ &- \langle N | \hat{\psi}^\dagger(1')\hat{\psi}(1) | N\rangle \langle N | \hat{\psi}^\dagger(2')\hat{\psi}(2) | N\rangle, \end{aligned} \tag{9}$$

and the Fourie transformed equation is then given by

$$\begin{aligned} \chi(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2; \omega) \\ &= \sum_{n\neq 0}\left[\frac{\langle N | \hat{\psi}^\dagger(1')\hat{\psi}(1) | N,n\rangle \langle N,n | \hat{\psi}^\dagger(2')\hat{\psi}(2) | N\rangle}{\omega - (E_{N,n} - E_N) + i0^+}\right. \\ &\left. - \frac{\langle N | \hat{\psi}^\dagger(2')\hat{\psi}(2) | N,n\rangle \langle N,n | \hat{\psi}^\dagger(1')\hat{\psi}(1) | N\rangle}{\omega + (E_{N,n} - E_N) - i0^+}\right] \end{aligned} \tag{11}$$

This indicates that the four-point linear response function in this special time-ordering corresponds to the linear-response of particle-hole pairs.

One can further introduce the independent-particle four-point linear-response function

$$\chi_{\text{IP}}(1,2;1',2') = -iG(1,1')G(2,2') \tag{12}$$

and the corresponding response function

$$\chi_{\text{IP}}(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2; \tau) = -iG(\boldsymbol{x}_1, \boldsymbol{x}'_2; \tau)G(\boldsymbol{x}_2, \boldsymbol{x}'_1; -\tau) \tag{13}$$

$$\chi_{\text{IP}}(\boldsymbol{x}_1, \boldsymbol{x}_2; \boldsymbol{x}'_1, \boldsymbol{x}'_2; \omega) = \sum_{i\leq N<a}\left[\frac{f_i^*(\boldsymbol{x}'_1)f_a(\boldsymbol{x}_1)f_a^*(\boldsymbol{x}'_2)f_i(\boldsymbol{x}_2)}{\omega - (\mathcal{E}_a - \mathcal{E}_i) + i0^+} - \frac{f_i^*(\boldsymbol{x}'_2)f_a(\boldsymbol{x}_2)f_a^*(\boldsymbol{x}'_1)f_i(\boldsymbol{x}_1)}{\omega + (\mathcal{E}_a - \mathcal{E}_i) - i0^+}\right]. \tag{14}$$

Having introduced the many-body Green's function, let us return to the discussion on the fluctuation dissipation theorem. The response function (Eqs. (9-10)) can be written as

$$\begin{aligned} \mathrm{i}\chi_\lambda(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) &= \langle \Psi^\lambda | T[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)\hat{n}^\lambda(\boldsymbol{r}_2 t_2)] | \Psi^\lambda \rangle - \langle \Psi^\lambda | T[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)] | \Psi^\lambda \rangle \langle \Psi^\lambda | T[\hat{n}^\lambda(\boldsymbol{r}_2 t_2)] | \Psi^\lambda \rangle \\ &= \langle \Psi^\lambda | T[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)\hat{n}^\lambda(\boldsymbol{r}_2 t_2)] | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}(\boldsymbol{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\boldsymbol{r}_2) | \Psi^\lambda \rangle \end{aligned} \tag{4.19}$$

If we set $t_2 = t_1 + 0^+$, the Heisenberg phase factor is canceled out and

$$\mathrm{i}\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) = \langle \Psi^\lambda | \hat{n}(\boldsymbol{r}_1)\hat{n}(\boldsymbol{r}_2) | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}(\boldsymbol{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\boldsymbol{r}_2) | \Psi^\lambda \rangle. \tag{4.20}$$

It is possible to derive similar equation for $\lambda = 0$, giving

$$\mathrm{i}\chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) = \langle \Phi | \hat{n}(\boldsymbol{r}_1)\hat{n}(\boldsymbol{r}_2) | \Phi \rangle - \langle \Phi | \hat{n}(\boldsymbol{r}_1) | \Phi \rangle \langle \Phi | \hat{n}(\boldsymbol{r}_2) | \Phi \rangle. \tag{4.21}$$

This makes it possible to write the two-body density correlation in terms of the response function as

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) = \mathrm{i}[\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) - \chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-)], \tag{4.22}$$

and using the Fourier transformed form as

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi \mathrm{i}} e^{i\omega 0^+} [\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) - \chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)], \tag{4.23}$$

which is known as the fluctuation dissipation theorem. When this is combined with the adiabatic connection formula, we get

$$E_\mathrm{c} = -\frac{1}{2}\int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi \mathrm{i}} e^{i\omega 0^+} \iint \frac{\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) - \chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

This is a particularly important formula which provides a practical way to compute the correlation functional in that we do not need the many-body wave function.

The problem is now reduced to the evaluation of the response function χ_λ. This can be done either by using the time-dependent DFT or the many-body perturbation within the GW approximation. For the moment, let us concentrate the former.

Time-dependent density functional theory (TD-DFT)

To explain the response function within DFT, I will briefly introduce TDDFT. According to Runge and Gross, there exists a one-to-one correspondence between the time-dependent density $n(\boldsymbol{r}, t)$ and the time-dependent effective potential $v_\mathrm{s}(\boldsymbol{r}, t)$, so that $n(\boldsymbol{r}, t)$ can be obtained by solving the time-dependent Kohn-Sham equation:

$$i\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r}, t) = \left[-\frac{1}{2}\nabla^2 + v_\mathrm{s}(\boldsymbol{r}, t)\right]\varphi_i(\boldsymbol{r}, t),$$

and

$$n(\boldsymbol{r}, t) = \sum_i^N |\varphi_i(\boldsymbol{r}, t)|^2$$

This is a natural extension of the Kohn-Sham DFT.

According to the many-body theory, in the linear response regime, the change in the density and change in the external potential can be related via the response function as

$$\delta n_\lambda(\boldsymbol{r},t)=\int_0^\infty dt'\int d\boldsymbol{r}'\,\chi_\lambda(\boldsymbol{r}t,\boldsymbol{r}'t')\delta v_{\mathrm{ext}}^\lambda(\boldsymbol{r}'t')$$

where

$$\chi_\lambda(\boldsymbol{r}t,\boldsymbol{r}'t')=\frac{\delta n(\boldsymbol{r}t)}{\delta v_{\mathrm{ext}}^\lambda(\boldsymbol{r}'t')}$$

the response function can be given (from the definition) as

$$\chi_\lambda(\boldsymbol{r},\boldsymbol{r}',\omega)=\sum_{m\neq 0}\left[\frac{\langle\Psi^\lambda|\hat{n}(\boldsymbol{r})|\Psi_m^\lambda\rangle\langle\Psi_m^\lambda|\hat{n}(\boldsymbol{r}')|\Psi^\lambda\rangle}{\omega-\omega_m+i0^+}-\frac{\langle\Psi^\lambda|\hat{n}(\boldsymbol{r}')|\Psi_m^\lambda\rangle\langle\Psi_m^\lambda|\hat{n}(\boldsymbol{r})|\Psi^\lambda\rangle}{\omega+\omega_m+i0^+}\right].$$

In TDDFT, the equations are replaced by those of a noninteracting system

$$\delta n(\boldsymbol{r},t)=\int_0^\infty dt'\int dr'\,\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}'t')\delta v_{\mathrm{s}}^\lambda(\boldsymbol{r}'t'),$$

$$\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}'t')=\frac{\delta n(\boldsymbol{r}t)}{\delta v_{\mathrm{s}}^\lambda(\boldsymbol{r}'t')},$$

and

$$\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega)=\sum_{kj}\frac{\varphi_k^{\lambda*}(\boldsymbol{r})\varphi_j^\lambda(\boldsymbol{r})\varphi_j^{\lambda*}(\boldsymbol{r}')\varphi_k^\lambda(\boldsymbol{r}')}{\omega-\omega_{jk}+i\eta}$$

The effective potential, $v_{\mathrm{s}}^\lambda(\boldsymbol{r}'t')=v_{\mathrm{ext}}^\lambda(\boldsymbol{r}'t')+v_{\mathrm{H}}(\boldsymbol{r}'t)+v_{\mathrm{xc}}^\lambda(\boldsymbol{r}'t')$, is related to the density via the exchange-correlation kernel K as

$$K_{\mathrm{xc}}^\lambda(\boldsymbol{r}t,\boldsymbol{r}'t')=\frac{\delta v_{\mathrm{xc}}^\lambda(\boldsymbol{r}t)}{\delta n(\boldsymbol{r}'t')},$$

so that

$$\delta v_{\mathrm{s}}^\lambda(\boldsymbol{r}t)=\delta v_{\mathrm{ext}}^\lambda(\boldsymbol{r}t)+\int \mathrm{d}\mathbf{r}'\frac{n(\boldsymbol{r}'t)}{|\mathbf{r}-\mathbf{r}'|}+\int d\boldsymbol{r}'dt'\mathrm{K}_{\mathrm{xc}}^\lambda(\boldsymbol{r}t,\mathbf{r}'\mathrm{t}')n(\boldsymbol{r}'t')$$

Since the same density response results in both cases, we get

$$\chi_\lambda(\boldsymbol{r}t,\boldsymbol{r}'t')=\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}'t')+\iiint\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}_1t_1)\left[\frac{\delta(t_1-t_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}+K_{\mathrm{xc}}^\lambda(\boldsymbol{r}_1t_1,\boldsymbol{r}_2t_2)\right]\chi_\lambda\,(\boldsymbol{r}_2t_2,\boldsymbol{r}'t')$$

Namely, once functional form for the exchange-correlation kernel is determined, we get the response function, with which one can calculate the correlation functional. The problem has not been solved by this, instead, the problem has been transferred to the construction of K_{xc}^λ, which is practically easier. Also, there is a way to construct it from a rigorous many-body theory.

Let us then introduce the many-body theory for constructing the response function. Again, we will follow the article written by Toulouse.

Self-energy

Returning to the equation of motion, which was derived above as

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2) = \delta(1,2) + h(1)G(1,2) + \mathrm{i}\int d3 v(1,3)G_2(1,3^+;2,3^{++}), \qquad (15)$$

let us introduce the self-energy operator. For this purpose, let us assume that we can find a solution for the following equation

$$\int d3\Sigma_{\mathrm{Hxc}}(1,3)G(3,2) = -i\int d3 v(1,3)G_2(1,3^+;2,3^{++}) \qquad (17)$$

or equivalently let us introduce the following quantity

$$\Sigma_{\mathrm{Hxc}}(1,4) = -i\int d3 v(1,3)G_2(1,3^+;2,3^{++})G^{-1}(2,4). \qquad (18)$$

Then, we obtain a formally closed form for the Green's function

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right]G(1,2) = \delta(1,2) + \int d3 v(1,3)G(3,2). \qquad (16)$$

This means that with the self-energy (Eq.(18)) we do not have to introduce the complicated multi-body Green's function.

Note that Green's function is given for independent electron approximation as

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right]G_{\mathrm{indep}}(1,2) = \delta(1,2) \qquad (19)$$

Using $G(1,2) = \int G_{\mathrm{indep}}(1,4)G_{\mathrm{indep}}^{-1}(4,3)G(3,2)$, we get

$$\int d3\left[G_{\mathrm{indep}}^{-1}(1,3) - \Sigma_{\mathrm{Hxc}}(1,3)\right]\mathrm{G}(3,2) = \delta(1,2) \qquad (20)$$

This is rewritten as

$$G(1,2) = G_{\mathrm{indep}}(1,2) + \iint G_{\mathrm{indep}}(1,3)\,\Sigma_{\mathrm{Hxc}}(3,4)G(4,2), \qquad (21)$$

or as

$$G^{-1}(1,2) = G_{\mathrm{indep}}^{-1}(1,2) - \Sigma_{\mathrm{Hxc}}(3,4). \qquad (22)$$

Equation (21) is known as the Dyson equation for the one-body Green's function.

Fourie transform is (assuming homogeneity of the system with respect to time) given as

$$[\omega - h(\boldsymbol{r}_1)]G(\boldsymbol{x}_1,\boldsymbol{x}_2;\omega) = \delta(\boldsymbol{x}_1,\boldsymbol{x}_2) + \int d\boldsymbol{x}_3\Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1,\boldsymbol{x}_3;\omega)G(\boldsymbol{x}_3,\boldsymbol{x}_2;\omega) \qquad (23)$$

Using the pole $\mathcal{E}_k$ and the wave function $f_k(\boldsymbol{x})$ of the Green's function, we can rewrite Eq. (23) at the pole as

$$[\mathcal{E}_k - h(\boldsymbol{r}_1)] f_k(\boldsymbol{x}_1) f_k^*(\boldsymbol{x}_2) = \int d\boldsymbol{x}_3\, \Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1, \boldsymbol{x}_3; \mathcal{E}_k) f_k(\boldsymbol{x}_3) f_k^*(\boldsymbol{x}_2) = 0, \qquad (24)$$

when there is no degeneracy. This can be further simplified as

$$h(\boldsymbol{r}_1) f_k(\boldsymbol{x}_1) + \int d\boldsymbol{x}_3\, \Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1, \boldsymbol{x}_3; \mathcal{E}_k) f_k(\boldsymbol{x}_3) = \mathcal{E}_k f_k(\boldsymbol{x}_1). \qquad (25)$$

If the imaginary part of the self-energy is zero, Eq. (25) is equivalent to a one-particle Schrödinger equation. Because of the imaginary part, however, it becomes similar to the equation with absorption potential, indicating decreasing amplitude of the wave function with time. It is known in some cases that the imaginary part is small for the energy states close to the Fermi level. So, Eq.(25) is called quasiparticle equation.

Note that the self-energy is apparently equivalent to the exchange-correlation potential of TD-DFT. It is therefore possible, in principle, to derive the exchange-correlation from the many-body theory although it is determined from empirical argument.

Exchange-correlation kernel from first principles

1. Green's function using the interaction representation

Suppose the system is perturbed by an external field $u(\boldsymbol{r})$, or

$$H'(t_1) = \int d1\, u(1) n(1).$$

The Green's function can be described using the interaction representation

$$G(1,1') = -\mathrm{i} \frac{\langle N | T[S\hat{\psi}(1)\hat{\psi}^\dagger(1')] | N \rangle}{\langle N | T[S] | N \rangle},$$

where S is the time-evolution operator in the interaction representation

$$S(t_a, t_b) = \exp\left[-\mathrm{i} \int_{t_b}^{t_a} dt_1 H'_I(1) \right]; \quad \mathrm{S} = \mathrm{S}(-\infty, \infty).$$

The two-body Green's function is also

$$G_2(1,1'; 2,2') = (-\mathrm{i})^2 \frac{\langle N | T[S\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(2')\hat{\psi}^\dagger(1')] | N \rangle}{\langle N | T[S] | N \rangle},$$

similarly to the one in the limit of $u \to 0$.

2. Equation of motion

The Green's function follows an equation of motion

$$\left[\mathrm{i} \frac{\partial}{\partial t_1} - h(1) - u(1) \right] G(1,1') + i \int d2\, v(1,2) G_2(1,1', 2^+, 2^{++}) = \delta(1,1').$$

When the Green's function is differentiated with respect to u, we get the equation known as Schwinger's trick

$$\frac{\delta G(1,1')}{\delta u(2)} = -G_2(1,1',2,2^+) + iG(1,1')G(2,2^+) = -G_2(1,1',2,2^+) + iG(1,1')\langle\hat{n}(2)\rangle.$$

With this, one can formally remove the two-body Green's function from the equation of motion:

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1) - u(1) - \int d2v(1,2)\langle\hat{n}(2)\rangle\right]G(1,1') - i\int d2v(1^+,2)\frac{\delta G(1,1')}{\delta u(2)} = \delta(1,1').$$

As we did above, we can define the self-energy operator

$$\begin{aligned}\Sigma(1,1') &= \int d2v(1,2)\langle\hat{n}(2)\rangle\,\delta(1,1') + i\iint d23\ v(1^+,2)\frac{\delta G(1,3)}{\delta u(2)}G^{-1}(3,1') \\ &\equiv \Sigma^{\mathrm{H}}(1,1') + \Sigma^{\mathrm{xc}}(1,1')\end{aligned}$$

so that the equation of motion can be rewritten as

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1) - u(1)\right]G(1,1') - i\int d2\Sigma(1,2)G(2,1') = \delta(1,1').$$

When unperturbed Green's function is defined from

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1)\right]G^{(0)}(1,1') = \delta(1,1'),$$

we have the equation of Dyson type

$$G(1,1') = G^{(0)}(1,1') + \iint d23\,G^{(0)}(1,2)\Sigma(2,3)G(3,1').$$

3. Self-energy

The self-energy operator has a form difficult to understand. Let us relate it physically understandable quantities. For this purpose, we define the total potential as a sum of the external potential and the Hartree-potential

$$V(1) = u(1) + \int d2v(1,2)\langle\hat{n}(2)\rangle$$

and consider the response of the Green's function to the change in the total potential;

$$-\frac{\delta \mathrm{G}^{-1}(1,2)}{\delta V(3)} \mapsto \Gamma(1,2;3)$$

The vertex function $\Gamma(1,2;3)$ can be rewritten in a Dyson form as

$$\Gamma(1,2;3) = \delta(1,2)\delta(2,3) + \iiint d4567\frac{\delta\Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)}\mathrm{G}(4,6)\mathrm{G}(7,5)\Gamma(6,7;3),$$

so that one may start the first order approximation from $\delta(1,2)\delta(2,3)$.

With the vertex, let us remove the unpleasant $\delta/\delta\mathrm{u}$ operator from the definition of the self-energy. The exchange-correlation part can be rewritten as

$$\mathit{\Sigma}^{\mathrm{xc}}(1,2)=\mathrm{i}\iint d3456\, v(1^+,3)\frac{\delta V(4)}{\delta u(3)}G(1,6)\mathit{\Gamma}(6,2;5).$$

Using the fact that the change in the total potential induced by the external potential is the dielectric function

$$\epsilon^{-1}(4,3)=\frac{\delta V(4)}{\delta u(3)}$$

and the fact that the dielectric function operated to the Coulomb potential is the screened Coulomb

$$W(1^+,4)=\int d3\ v(1^+,3)\epsilon^{-1}(4,3)$$

Σ^{xc} can be rewritten as

$$\Sigma^{\mathrm{xc}}(1,2)=\ \mathrm{i}\iint d56\, W(1^+,3)G(1,6)\Gamma(6,2;5).$$

To remove the $\delta/\delta\mathrm{u}$ operator from the screened Coulomb, it is rewritten as

$$\begin{aligned}W(1^+,2)=v(1^+,2)+\int d34\ v(1^+,4)\frac{\delta G(4,4^+)}{\delta V(5)}\frac{\delta V(5)}{\delta u(3)}v(3,2)\\ =v(1^+,2)+\int d34\ v(1^+,4)\frac{\delta G(4,4^+)}{\delta V(5)}W(5,2)\\ =v(1^+,2)+\int d34\ v(1^+,4)\frac{\delta\langle\hat{\rho}(2)\rangle}{\delta V(5)}W(5,2)\end{aligned}$$

and then, the derivative appearing in the last line, which is the polarization, is rewritten using the vertex function as

$$P(1,2)=\mathrm{i}\int d34\, G(1,3)\frac{\delta G^{-1}(3,4)}{\delta V(2)}G(4,1^+)=-i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2).$$

Then, we can obtain a Dyson equation for the screened Coulomb as

$$W(1^+,2)=v(1^+,2)+\int d34\ v(1^+,4)P(2,5)W(5,2).$$

4. Hedin's equation

Finally, we arrive at a closed set of equations called Hedin's equation

$$G(1,2)=G^0(1,2)+\int d34G^0(1,3)\Sigma(3,4)G(4,2)$$
$$\Sigma^{\mathrm{xc}}(1,2)=i\int d34W(1^+,3)G(1,4)\Gamma(4,2;3)$$
$$P(1,2)=-i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$
$$W(1,2)=V_C(1,2)+\int d34V_C(1,3)P(3,4)W(4,2)$$
$$\Gamma(1,2;3)=\delta(1,2)\delta(1,3)+\int d4567\frac{\delta\Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7;3)$$

By self-consistently solve them, one can rigorously obtain the Green's function. When the vertex function is approximated as the product of delta functions, it corresponds to approximating as $\Sigma^{\mathrm{xc}}(1,2) = i\int d34W(1^{+},3)G(1,4)$. This is the reason why it is called the GW approximation. This approximation also means to taking $P(1,2) = -i\int d34\, G(1,3)G(4,1^{+})$, which indicates two particles are propagating independently. As a higher order approximation, one can use the first order approximation

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4567\frac{\delta\Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)}G(4,6)G(7,5)$$

to obtain the polarization. The resulting set of equations is called the GW + Bethe Salpeter equation.

To describe the equation, it is convenient to use the four-point response function defined above

$$\chi(1,2;1',2') = L(1,1',2,2') = \mathrm{i}G_2(1,1',2,2') - G(1,1')G'2',2).$$

It can be derived by Schwinger that this quantity is given as a response of the Green's function $G(1,1')$ perturbed by a nonlocal external potential $u(2,2)$ as

$$L(1,1',2,2') = -\mathrm{i}\frac{\delta \mathrm{G}(1,1')}{\delta \mathrm{u}(2,2)}.$$

Using the identity of the functional derivative,

$$\frac{\delta F(1,1')}{\delta G(3)} = -\int F(1,3)\frac{\delta F^{-1}(3,3')}{\delta G(2)}F(3',1')d3d3',$$

we obtain

$$\frac{\delta \mathrm{G}(1,1')}{\delta \mathrm{u}(2,2')} = -\int G(1,3)G(3',1')\frac{\delta \mathrm{G}^{-1}(3,3')}{\delta \mathrm{u}(2,2')}d3d3'.$$

When this is substituted with the Dyson equation

$$G^{-1}(3,3') = G_0^{-1}(3,3') - u(3,3') - \Sigma(3,3'),$$

We obtain

$$\frac{\delta \mathrm{G}(1,1')}{\delta \mathrm{u}(2,2')} = \mathrm{G}(1,2)\mathrm{G}(2',1) + \int G(1,3)G(3',1')\frac{\delta\Sigma(3,3')}{\delta \mathrm{u}(2,2')}d3d3'$$

$$= \mathrm{G}(1,2)\mathrm{G}(2',1) + \int G(1,3)G(3',1')\frac{\delta\Sigma(3,3')}{\delta \mathrm{G}(4,4')}\frac{\delta \mathrm{G}(4,4')}{\delta \mathrm{u}(2,2')}d3d3'd4d4'.$$

The first term in the left-hand side, or the product of the Green's functions, is regarded as the four-point response function within the independent pair approximation. Therefore, it will be denoted as $L_0(1,1',2,2')$. The second term contains the derivative of the self-energy, which will be denoted as

$$K(3,3',4,4') = \mathrm{i}\frac{\delta\Sigma(3,3')}{\delta \mathrm{G}(4,4')}.$$

This quantity is the electron-hole interaction kernel because it relates the non-interacting response function with the interacting one as

$$L(1,1',2,2') = l_0(1,1',2,2') + \int L_0(1,1',3,3')K(3,3',4,4')L(4,4',2,2')d3d3'd4d4'.$$

The kernel K can be decomposed into the Hartree and exchange-correlation contributions. The former

$$K^{\mathrm{x}}(3,3',4') \equiv i\frac{\delta\Sigma^{\mathrm{H}}(3,3')}{\delta \mathrm{G}(4,4')}$$

is called bare Coulomb exchange interaction and can be described as

$$K^{\mathrm{x}}(3,3',4') = \delta(3,3')\delta(4,4')v(3,4).$$

While the latter is given within the GW approximation as

$$i\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')} = -\delta(3,4)\delta(3',4')W(3^+,3') - G(3,3')\frac{\delta \mathrm{W}(3^+,3')}{\delta \mathrm{G}(4,4')}.$$

The functional derivative, the second term in the right-hand side, can be removed by using the polarization, $W = v + vPW$, which provides the relation $\delta W/\delta G = W\,\delta P/\delta G\,W$ as

$$i\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')} = -\delta(3,4)\delta(3',4')W(3^+,3') - \int G(3,3')W(3^+,5)\frac{\delta P(5,6)}{\delta G(4,4')}W(6,3')d5d6.$$

Using the approximation $P = -GG$,

$$\begin{aligned} i\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')} &= -\delta(3,4)\delta(3',4')W(3^+,3') \\ &\quad + \mathrm{i}\int G(3,3')W(3^+,5)\frac{\delta\big(G(5,6)G(6,5^+)\big)}{\delta G(4,4')}W(6,3')d5d6, \end{aligned}$$

and further,

$$\begin{aligned} i\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')} &= -\delta(3,4)\delta(3',4')W(3^+,3') + iW(3^+,4)G(4',4^+)W(4',3') \\ &\quad + iW(3^+,4')G(4',4^+)W(4,3'). \end{aligned}$$

The first term is called the direct term, and the second and third terms are called second-order correction terms.

$$K^{\mathrm{x}}(3,3',4,4') = \delta(3,3')\delta(4,4')v(3,4)$$

$$K^{\mathrm{d}}(3,3',4,4') = -\delta(3,4)\delta(3'4')W(3^+,3')$$

$$K'^{(3,3',4,4')} = -G(3,3')\frac{\delta W(3,3^+)}{\delta G(4,4')}.$$

It is important that this GW + Bethe Salpeter equation can be rewritten using the Kohn-Sham orbitals as basis. The resulting equation is formally the same as the response function appeared above in TD-DFT,

$$\chi(rt,r't') = \chi_{\mathrm{KS}}(rt,r't') + \iiint \chi_{KS}(rt,r_1t_1)\left[\frac{\delta(t_1-t_2)}{|r_1-r_2|} + K_{\mathrm{xc}}(r_1t_1,r_2t_2)\right]\chi(r_2t_2,r't').$$

When we take the standpoint that the response function is given as a functional of the electron density through the KS orbitals, this is a density functional theory with advanced form for the exchange-correlation.

Direct random phase approximation

Let us go back to the density functional theory again. One of the crude approximations to the response function was to take the direct term only, which is within the adiabatic connection path

$$K^{\lambda}_{\mathrm{Hxc}}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) \simeq K^{\lambda}_{\mathrm{H}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \lambda v(\boldsymbol{r}_1,\boldsymbol{r}_2). \tag{4.28}$$

When this is used, the resulting equation for the response function is

$$\chi_{\lambda}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) = \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) + \lambda \iiint \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega) v(\boldsymbol{r}_3,\boldsymbol{r}_4)\chi_{\lambda}(\boldsymbol{r}_4,\boldsymbol{r}_2;\omega). \tag{4.29}$$

By this we can define the correlation functional within this approximation called direct RPA as

$$\begin{aligned}E_{\mathrm{c}}^{\mathrm{dRPA}} = -\frac{1}{2}\int_0^1 d\lambda \int_{\infty}^{\infty} \frac{d\omega}{2\pi \mathrm{i}} e^{-\mathrm{i}\omega 0^+}\ [\lambda \iiint \frac{\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega)\chi_0(\boldsymbol{r}_4,\boldsymbol{r}_2;\omega)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \\ + \lambda^2 \iiint \frac{\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega)\chi_0(\boldsymbol{r}_4,\boldsymbol{r}_5;\omega)\chi_0(\boldsymbol{r}_6,\boldsymbol{r}_2;\omega)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4||\boldsymbol{r}_5-\boldsymbol{r}_6|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 d\boldsymbol{r}_5 d\boldsymbol{r}_6 \\ + \cdots]\ \ (4.30)\end{aligned}$$

Practical formulation of dRPA

Equation (4.29) can be expressed using the four-point response function as

$$\begin{aligned}&\mathrm{i}\chi_{\lambda}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}'_1,\boldsymbol{x}'_2;\tau) \\ &\quad = \langle \Psi^{\lambda} | T[\hat{n}_1^{\lambda}(\boldsymbol{x}_1,\boldsymbol{x}'_1;t_1)\hat{n}_1^{\lambda}(\boldsymbol{x}_2,\boldsymbol{x}'_2;t_2)] | \Psi^{\lambda} \rangle \\ &\quad - \langle \Psi^{\lambda} | \hat{n}_1^{\lambda}(\boldsymbol{x}_1,\boldsymbol{x}'_1;t_1) | \Psi^{\lambda} \rangle \langle \Psi^{\lambda} | \hat{n}_1^{\lambda}(\boldsymbol{x}_2,\boldsymbol{x}'_2;t_2) | \Psi^{\lambda} \rangle.\end{aligned} \tag{4.34}$$

Within dRPA the Dyson equation for the response function is

$$\begin{aligned}&\chi_{\lambda}^{\mathrm{dRPA}}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}'_1,\boldsymbol{x}'_2;\omega) \\ &= \chi_0(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}'_1,\boldsymbol{x}'_2;\omega) \\ &+ \iiint d\boldsymbol{x}_3 d\boldsymbol{x}_4 d\boldsymbol{x}_5 d\boldsymbol{x}_6 \chi_0(\boldsymbol{x}_1,\boldsymbol{x}_4,\boldsymbol{x}'_1,\boldsymbol{x}_3;\omega) K_{\mathrm{H}}^{\lambda}(\boldsymbol{x}_3,\boldsymbol{x}_6;\boldsymbol{x}_4,\boldsymbol{x}_5)\, \chi_{\lambda}^{\mathrm{dRPA}}(\boldsymbol{x}_5,\boldsymbol{x}_2,\boldsymbol{x}_6,\boldsymbol{x}'_2;\omega)\end{aligned} \tag{4.36}$$

with the kernel being given by

$$K_{\mathrm{H}}^{\lambda}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}'_1,\boldsymbol{x}'_2) = \lambda v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\delta(\boldsymbol{x}_1-\boldsymbol{x}'_1)\delta(\boldsymbol{x}_2-\boldsymbol{x}'_2)$$

Note that the non-interacting kernel can be given by the KS orbitals as

$$\chi_0(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1',\boldsymbol{x}_2';\omega)=\sum_{i\leq N<a}\left[\frac{\phi_i^*(\boldsymbol{x}_1')\phi_a(\boldsymbol{x}_1)\phi_a^*(\boldsymbol{x}_2')\phi_i(\boldsymbol{x}_2)}{\omega-(\varepsilon_a-\varepsilon_i)+\mathrm{i}0^+}-\frac{\phi_i^*(\boldsymbol{x}_2')\phi_a(\boldsymbol{x}_2)\phi_a^*(\boldsymbol{x}_1')\phi_i(\boldsymbol{x}_1)}{\omega+(\varepsilon_a-\varepsilon_i)-\mathrm{i}0^+}\right]$$

Now we take a basis representation. The basis is formed using the combined occupied and unoccupied orbitals as

$$f_{ia}(\boldsymbol{x}_1,\boldsymbol{x}_1')=\phi_i^*(\boldsymbol{x}_1')\phi_a(\boldsymbol{x}_1)$$
$$f_{ai}(\boldsymbol{x}_1,\boldsymbol{x}_1')=\phi_a^*(\boldsymbol{x}_1')\phi_i(\boldsymbol{x}_1).$$

Then χ_0 can be expanded as

$$\chi_0(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1',\boldsymbol{x}_2';\omega)\sum_{pq}[\chi_0]_{pq}f_p(\boldsymbol{x}_1,\boldsymbol{x}_1')f_q^*(\boldsymbol{x}_2,\boldsymbol{x}_2')$$

where

$$[\chi_0(\omega)]_{ia,jb}=\frac{\delta_{ij}\delta_{ab}}{\omega-(\varepsilon_a-\varepsilon_i)+\mathrm{i}0^+}$$

$$[\chi_0(\omega)]_{ai,bj}=\frac{\delta_{ij}\delta_{ab}}{\omega+(\varepsilon_a-\varepsilon_i)-\mathrm{i}0^+}$$

$$[\chi_0(\omega)]_{ia,bj}=[\chi_0(\omega)]_{ai,jb}=0.$$

Therefore, in a matrix representation

$$(\chi_0)^{-1}(\omega)=-\left[\begin{pmatrix}\boldsymbol{\Delta\varepsilon} & \mathbf{0}\\ \mathbf{0} & \boldsymbol{\Delta\varepsilon}\end{pmatrix}-\omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{-1}\end{pmatrix}\right] \tag{4.39}$$

with

$$\Delta\varepsilon_{ia,jb}\equiv(\varepsilon_a-\varepsilon_i)\delta_{ij}\delta_{ab}.$$

Then

$$\left(\chi_\lambda^{\mathrm{dRPA}}\right)^{-1}(\omega)=-\left[\begin{pmatrix}\mathbf{A}_\lambda & \boldsymbol{B}_\lambda\\ \boldsymbol{B}_\lambda^* & \mathbf{A}_\lambda^*\end{pmatrix}-\omega\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{-1}\end{pmatrix}\right] \tag{4.40}$$

with

$$(A_\lambda)_{ia,jb}=\Delta\varepsilon_{ia,jb}+\lambda\langle\phi_a\phi_j|\phi_i\phi_b\rangle$$
$$(B)_{ia,jb}=\lambda\langle\phi_a\phi_b|\phi_i\phi_j\rangle. \tag{4.41}$$

To take the inverse in Eq. (4.40), we solve the generalized eigenvalue problem

$$\begin{pmatrix}\mathbf{A}_\lambda & \boldsymbol{B}_\lambda\\ \boldsymbol{B}_\lambda^* & \mathbf{A}_\lambda^*\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}\\ \boldsymbol{Y}_{n,\lambda}\end{pmatrix}=\omega_n^\lambda\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{-1}\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}\\ \boldsymbol{Y}_{n,\lambda}\end{pmatrix} \tag{4.42}$$

Under the normalization condition for the eigenvectors (X ,Y), the response function is

$$\boldsymbol{\chi}_\lambda^{\mathrm{dRPA}}(\omega)=\sum_n\left[\frac{1}{\omega-\omega_n^\lambda+i0^+}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}\\ \boldsymbol{Y}_{n,\lambda}\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^\dagger & \boldsymbol{Y}_{n,\lambda}^\dagger\end{pmatrix}-\frac{1}{\omega+\omega_n^\lambda-i0^+}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^*\\ \boldsymbol{Y}_{n,\lambda}^*\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^{*\dagger} & \boldsymbol{Y}_{n,\lambda}^{*\dagger}\end{pmatrix}\right],$$

and the correlation part of the two-body density matrix is then

$$\boldsymbol{n}_{2,\mathrm{c}}^{\lambda,\mathrm{dRPA}}=-\int_\infty^\infty\frac{d\omega}{2\pi\mathrm{i}}e^{\mathrm{i}\omega0^+}[\boldsymbol{\chi}_\lambda(\omega)-\boldsymbol{\chi}_0(\omega)]=\sum_n\left[\begin{pmatrix}\boldsymbol{Y}_{n,\lambda}^*\boldsymbol{Y}_{n,\lambda}^{*\dagger} & \boldsymbol{Y}_{n,\lambda}^*\boldsymbol{X}_{n,\lambda}^{*\dagger}\\ \boldsymbol{X}_{n,\lambda}^*\boldsymbol{Y}_{n,\lambda}^{*\dagger} & \boldsymbol{X}_{n,\lambda}^*\boldsymbol{X}_{n,\lambda}^{*\dagger}\end{pmatrix}-\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{1}\end{pmatrix}\right]$$

Therefore, the correlation functional is given by

$$E_{\mathrm{c}}^{\mathrm{dRPA}} = \frac{1}{2}\int_0^1 d\lambda \sum_{ij\leq N<ab} \sum_n \langle \phi_i\phi_b|\phi_a\phi_j\rangle \left(Y_{n,\lambda}\right)_{ia}^{*}\left(Y_{n,\lambda}\right)_{jb} + \langle \phi_i\phi_j|\phi_a\phi_b\rangle \left(X_{n,\lambda}\right)_{ia}^{*}(X)_{jb}$$

$$+ \langle \phi_a\phi_b|\phi_i\phi_j\rangle \left(X_{n,\lambda}\right)_{ia}^{*}\left(Y_{n,\lambda}\right)_{jb} + \langle \phi_i\phi_b|\phi_a\phi_j\rangle \left[(X)_{ia}^{*}\left(X_{n,\lambda}\right)_{jb} - \delta_{ij}\delta_{ab}\right].$$

This is the formulation within the direct RPA. There are other formulations as well depending on how the λ integration is done efficiently by introducing approximations/assumptions.

Most of the dRPA calculations are done non-self-consistently using a lower-level electron density although self-consistent calculation can be done using the optimized effective potential scheme. With this, we can incorporate the van der Waals interaction. Yet, this scheme is not free-from the self-interaction, that will affect insulators more significantly. To overcome it, one can add the exchange to the direct term as

$$K_{\mathrm{Hxc}}^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) \simeq K_{\mathrm{Hx}}^{\lambda}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \lambda v(\boldsymbol{r}_1, \boldsymbol{r}_2) + \lambda K_x(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega).$$

This approach is found to correct the problem only minorly. It is thus necessary to go beyond the RPA approach by adding terms that include the vertex correction.

Nonadiabatic coupling of electrons and nuclei (ions)

Here we consider the whole system, consisting of electrons and ions, quantum mechanically although ions have been treated classically so far. We will go beyond the Born-Oppenheimer (BO) approximation here. By the way, what was the BO approximation?

BO approximation is explained as originating from large difference in mass between an electron and a nucleus; even for proton the ratio is 1/1700. For heavier elements, the ratio amounts to that of Earth over Sun. It is no wonder to decouple the motion of nuclei from that of electrons. Even though BO approximation will be generally valid to first order approximation, there are phenomena related to breaking down of BO approximation. Such occurs for chemical reactions, electronic friction, and so on.

Now let us discuss it quantitatively using the BO theory.

As the starting point, let us consider the system with

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V(R, r)$$

where an electron with coordinate r and mass m and a nucleus with coordinate R and mass M is interacting via $V(R, r)$. The time-dependent Schrödinger equation is

$$i\hbar\partial_t\Psi(r,R,t) = \hat{H}\Psi(r,R,t).$$

When $M \gg m$, naïve approximation is to neglect the first term in the Hamiltonian and treat the nuclear coordinate classically. It can be also assumed that the nuclear velocity is much smaller than the electronic one, by which the electrons will have enough time to deexcite to the ground state via coupling to environmental degrees of freedom, like electromagnetic field, phonon, and so on. In that case, one need to solve a static equation

$$\hat{H}_{el}\big(R(t)\big) = -\frac{\hbar^2}{2m}\nabla_r^2 + V\big(r;R(t)\big)$$

$$\hat{H}_{\mathrm{el}}\Psi_{\mathrm{el}}\big(r;R(t)\big) = E_{el}\big(R(t)\big)\Psi_{\mathrm{el}}\big(r;R(t)\big)$$

where $E_{el}\big(R(t)\big)$ is the ground state energy of electrons for a given configuration of nuclei, which is usually called the BO potential energy surface. The classical nuclei will evolve with time according to the Newton equation

$$M\partial_t^2 R(t) = -\nabla_{\mathrm{R}} E_{el}\big(R(t)\big).$$

Let us derive this more formally. To do this, we prepare a complete set of the electronic Hamiltonian and expand the whole wave function as

$$\Psi(r,R,t) = \sum_n \chi_n(R,t)\psi_n(r;R),$$

where

$$\hat{H}_{\mathrm{el}}\psi_{\mathrm{n}}(r;R) = E_n(R)\psi_n(r;R).$$

Note that the nuclear coordinate is treated quantum mechanically through the nuclear wave function $\chi_n(R,t)$, which is introduced as the expansion coefficient. $\psi_n(r;R)$ is time-independent and is given as a function of parameter R; time-dependence is considered only through χ.

The nuclear wave function follows an equation of motion, which can be straightforwardly obtained by applying the whole wave function into the starting time-dependent Schrödinger equation

$$i\hbar\partial_t\chi_m(R,t) = \left[-\frac{\hbar^2}{2M}\nabla_R^2 + E_m(R)\right]\chi_m(R,t)$$

$$-\frac{\hbar^2}{M}\sum_n \langle\psi_m|\nabla_R|\psi_n\rangle\nabla_R\chi_n(R,t) - \frac{\hbar^2}{2M}\sum_n \langle\psi_m|\nabla_R^2|\psi_n\rangle\chi_n(R,t) \qquad (1).$$

When the first term in the right-hand side is larger than the second and third terms, the nuclear wave function of m-th excited state $\chi_m(R,t)$ follows quantum equation of motion given by the corresponding potential surface $E_\mathrm{m}(R)$. Then $\chi_m(R,t)$ can be regarded as the wave packet. The centroid of $\chi_m(R,t)$ follows the Newton equation. This corresponds to the BO approximation.

Because of the second and third terms, the nuclear wave packets are interfering with each other. The BO approximation thus breaks down. The second term represents a coupling through the first-order nonadiabatic coupling (NAC) vector

$$\langle\psi_m|\nabla_R|\psi_n\rangle$$

and the third term represents the coupling through the second-order NAC $\langle\psi_m|\nabla_R^2|\psi_n\rangle$.

The first-order NAC vector can be rewritten as

$$\langle\psi_m|\nabla_R|\psi_n\rangle = \frac{\langle\psi_m|(\nabla_R\hat{H})|\psi_n\rangle}{E_\mathrm{n} - E_m}.$$

This indicates that NAC should be very large when there is a degeneracy of the BO surface. When the numerator is non-zero, the coupling diverges at the degenerate point, which is usually called as crossing point. The BO surfaces generally looks like a Dirac cone of graphene because of linear behavior of the BO surfaces. Therefore, the crossing point is sometimes called as a conical intersection.

The breakdown of the BO surfaces can happen at the crossing point even when the nuclear mass is large. For metals, the crossing should occur. For example, when a charged particle approaches a metal surface, the ground state will be mixed with excited states though which energy transfer occurs from the particle to the surface. The particle is then decelerated. This phenomenon is called electronic friction. This contrasts the friction generally occurring for insulators, where the energy transfer occurs from the particle to phonon.

On the other hand, the coupling $\langle\psi_m|\nabla_R|\psi_n\rangle$ is generally large for insulators although the crossing does not usually occur between the ground state and the first-excited state; this is reflected from the large electron-phonon coupling. The crossing, however, can occur between two excited states. Therefore, the mixing occurs in excited states dynamics. Suppose there is a potential surface that may lead to a dissociation of a molecule and another one that may not. Depending on the velocity of the wave packet $\nabla_R\chi_n(R,t)$, the second term in the Hamiltonian (Eq. (1)) can be large or small; the faster the velocity the larger the coupling is. This explains behavior of fast chemical reaction occurring after photo-excitation.

How to access the NAC vector

To get the value of NAC vector, one needs to evaluate the change of the many-body wave function (eigenstate of the electronic Hamiltonian) with respect to displacement of nucleus, $\langle\psi_m|\nabla_R|\psi_n\rangle$, which is usually too difficult to achieve. In this context, let us recall the equation

$$\langle\psi_m|\nabla_R|\psi_n\rangle = \frac{\langle\psi_m|(\nabla_R\hat{H})|\psi_n\rangle}{E_n - E_m} = \frac{\left\langle\psi_m\middle|\nabla_R\left(\frac{-Ze^2}{|r-R|}\right)\middle|\psi_n\right\rangle}{E_n - E_m} \equiv \frac{\langle\psi_m|h(R)|\psi_n\rangle}{E_n - E_m},$$

where $h(r;R) \equiv \nabla_R\left(\frac{-Ze^2}{|r-R|}\right)$. Let us then compare it with the density response induced by the perturbation $V_{\mathrm{ext}}(r,\omega) = h(r;R)e^{i\omega t}$, that is,

$$\delta\rho(r,\omega) = \int \chi(r,r',\omega)V_{\mathrm{ext}}(r',\omega)dr'$$

The response function is given by

$$\chi(r,r',\omega) = \sum_n\left[\frac{\langle\psi_0|\hat{\rho}(r)|\psi_n\rangle\langle\psi_n|\hat{\rho}(r')|\psi_0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle\psi_0|\hat{\rho}(r')|\psi_n\rangle\langle\psi_n|\hat{\rho}(r)|\psi_0\rangle}{\omega+(E_n-E_0)+i\eta}\right],$$

where $\hat{\rho}(r) = \sum_{\alpha=1}^{N}\delta(r-r_\alpha)$. When taking $\int dr\,\delta\rho(r,\omega)V_{\mathrm{ext}}(r,\omega)$, the resulting quantity is proportional to

$$\sum_n\left[\frac{\langle\psi_0|V_{\mathrm{ext}}|\psi_n\rangle\langle\psi_n|V_{\mathrm{ext}}|\psi_0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle\psi_0|V_{\mathrm{ext}}|\psi_n\rangle\langle\psi_n|V_{\mathrm{ext}}|\psi_0\rangle}{\omega+(E_n-E_0)+i\eta}\right]$$
$$= \sum_n\left[\frac{\langle\psi_0|h(R)|\psi_n\rangle\langle\psi_n|h(R)|\psi_0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle\psi_0|h(R)|\psi_n\rangle\langle\psi_n|h(R)|\psi_0\rangle}{\omega+(E_n-E_0)+i\eta}\right]$$

of which the numerator is square of the NAC vector. This indicates that the NAC vector can be given by the susceptibility (correlation) of $h(R)$.

According to the time-dependent DFT, this can be given via the Dyson equation

$$\chi(r,r',\omega) = \chi_{KS}(r,r',\omega) + \int dr_1dr_2\,\chi_{KS}(r,r_1,\omega)K_{\mathrm{HXC}}(r_1,r_2,\omega)\chi(r_2,r',\omega),$$

where

$$K_{\mathrm{HXC}}(r_1,r_2,\omega) = \frac{1}{|r_1-r_2|} + f_{\mathrm{xc}}(r_1,r_2,\omega)$$

and

$$\chi_{KS}(r,r',\omega) = 2\sum_{ia}\left[\frac{\varphi_i^*(r)\varphi_a(r)\varphi_a^*(r')\varphi_i(r')}{\omega-(\varepsilon_a-\varepsilon_i)+\mathrm{i}\eta} - \frac{\varphi_a^*(r)\varphi_i(r)\varphi_i^*(r')\varphi_a(r')}{\omega+(\varepsilon_a-\varepsilon_i)-\mathrm{i}\eta}\right],$$

where i (a) runs over all the occupied (unoccupied) states. (Practically, one cannot take all the unoccupied states into account. One needs to introduce a cutoff). Therefore, by computing the susceptibility using the response function of TD-DFT, one can obtain the value of NAC vector. There is a known compact form for the response function, known as Casida equation, which can be used to conveniently. TD-DFT is accessible by Quantum

Espresso as well as may quantum chemical software packages like Gaussian.

Recall that the TD-DFT equation was derived from the response of the Kohn-Sham artificial system to the change in the effective potential

$$\delta\rho(r,t) = \int \chi_{KS}(rt,r't')\delta v_{\mathrm{eff}}(r't')dr' = \int \chi_{KS}(rt,r't')(\delta v_{\mathrm{ext}}(r't') + \delta v_{\mathrm{HXC}}(r't'))dr'$$

$$= \int \chi_{KS}(rt,r't')(\delta v_{\mathrm{ext}}(r't') + f_{\mathrm{HXC}}(r't',r''t'')\delta v_{\mathrm{ext}}(r''t''))dr',$$

which is Fourier transformed to the previous equation. The quantity f_{HXC}, or the Hartree exchange-correlation kernel, is a functional of the time-dependent density. Note that the adiabatic approximations (or ω-independent approximations) are usually adopted. Note also that the kernel formally plays a role of describing the interacting electrons and holes as does the exchange-correlation self-energy in the theory of Hedin.

It is worth mentioning that the TD-DFT has been shown within the linear response scheme. But the importance of TD-DFT is in the fact that non-linear response can be accessed despite its limited accuracy originated from using approximate functionals. The linear response means a linear deviation from the ground state, which is generally invalid for representing the excited state density. The excited-state of a small molecules, for example, has a density that is very different from that of the ground state. The excitation is no more a small perturbation to the system. In that case, one should alternatively follow a real-time evolution of electrons, which can be achieved by integrating the time-dependent Kohn-Sham equation with respect to time.

The simplest expansion formula like

$$\mathrm{i}\hbar\frac{\varphi_n(t+\Delta t) - \varphi_n(t-\Delta t)}{2\Delta t} = \left(-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(rt)\right)\varphi_n(t)$$

is not very appropriate in this case because this does not guarantee orthonormalization of the Kohn-Sham orbitals. In this context, it is convenient to use

$$\varphi_n(t+\Delta t) = \exp\left[-\frac{1}{\mathrm{i}\hbar}\left(-\frac{1}{2}\nabla^2 + V_{eff}(rt)\right)\Delta t\right]\varphi_n(t)$$

$$\simeq \exp\left[-\frac{1}{2\mathrm{i}\hbar}\left(-\frac{1}{2}\nabla^2\right)\Delta t\right]\exp\left[-\frac{1}{\mathrm{i}\hbar}V_{eff}(rt)\Delta t\right]\exp\left[-\frac{1}{2\mathrm{i}\hbar}\left(-\frac{1}{2}\nabla^2\right)\Delta t\right]\varphi_n(t)$$

which guarantees the orthonormalization and thus advantageous for parallel computation.

When applying the classical approximation to nuclei as

$$i\hbar\,\partial_t\Psi_{\mathrm{el}}\big(r;R(t)\big)=\widehat{H}_{\mathrm{el}}\Psi_{\mathrm{el}}\big(r;R(t)\big)$$
$$M\partial_t^2R(t)=-\nabla_{\mathrm{R}}E_{el}\big(R(t)\big)$$

this coupled electronic and nuclear equation is called Ehrenfest equation of motion. This is a kind of mean-field approximation to the coupling of electrons and ions. In integrating this coupled electron-nucleus equation, one will encounter a problem of very different time-scale for the electronic and nuclear motion. The large difference in the time-scale makes the numerical approach very unstable.

It is worth mentioning that the mixed classical-quantum approach like the Ehrenfest is known to introduce a fundamental problem; as note in many textbook of quantum mechanics, nuclear force derived thereby can be meaningless. Nuclear motion will be driven by the "force from electron" averaged over quantum states of electrons, which needs to be handled carefully. When, for example, there are two electronic states for which a nucleus will feel a dissociative force and a binding force, respectively. The nucleus will feel just an averaged force although, in proper quantum mechanical approach, the nuclear wave functions of dissociative and bound character should be used to describe the nuclear state. For a system of very small degrees of freedom, there are ways to avoid such problem but is not practical for large systems.

There are movies on the Ehrenfest TD-DFT simulations, for example, on the internet.
https://figshare.com/articles/Physical_Factors_Affecting_Charge_Transfer_at_the_Pe_COOH_TiO_sub_2_sub_Anatase_Interface/2238757
One can observe a charge-transfer phenomenon that occurs between the adsorbate molecule Pe-COOH to a titania surface. The authors investigated how the charge transfer dynamics is affected by nuclear motion.

Quantum mechanical behavior of nuclei

Although nuclei are heavy, they behave as a classical particle at high temperatures. However, this is not always the case. Especially for hydrogen, or proton, the quantum effect is negligibly small. To take the quantum effect into account, at least approximately, one can use the path integral method.

For this purpose, let us start from the Hamiltonian

$$\widehat{H}=\sum_I\frac{\widehat{P}_I^2}{2M}+H_e(\hat{r},\hat{p};\hat{R})$$

and adiabatic states $|\psi_i(R)\rangle$. By decoupling the whole system into electronic and nuclear states as

$$|\psi_i(R)\rangle|R\rangle \equiv |i,R\rangle$$

the following equation is assumed to hold

$$H_e\left(\hat{r},\hat{p};\hat{R}\right)|\psi_i(R)\rangle|R\rangle = E_i(R)|\psi_i(R)\rangle|R\rangle.$$

We are interested in an equilibrium density at temperature T. Then we will derive a formula for the partition function

$$Z = \mathrm{Tr}\left[\exp\left(-\beta\hat{H}\right)\right] = \int dR\sum_i\left\langle i,R\right|\exp\left(-\beta\hat{H}\right)\left|i,R\right\rangle$$

When the exponential is partitioned into P parts by inserting the identity

$$\int dR_i\sum_i|iR\rangle\langle iR|,$$

we get

$$Z = \int dR_1\cdots dR_P\sum_{i_1,\cdots,i_P}\left\langle i,R\right|\exp\left(-\frac{\beta}{P}\hat{H}\right)\left|i_P,R_P\right\rangle$$

$$\times\left\langle i_P,R_P\right|\exp\left(-\frac{\beta}{P}\hat{H}\right)\left|i_{P-1},R_{P-1}\right\rangle\cdots\left\langle i_1,R_1\right|\exp\left(-\frac{\beta}{P}\hat{H}\right)\left|i,R\right\rangle$$

Then we need to evaluate terms like

$$\rho(s,s-1;\tau) \equiv \left\langle i_s,R_s\right|\exp\left(-\frac{\beta}{P}\hat{H}\right)\left|i_{s-1},R_{s-1}\right\rangle$$

This can be approximated as

$$\rho(s,s-1;\tau) \simeq \langle\psi_0(R_s)|\psi_0(R_{s-1})\rangle\left\langle R_s\right|\exp\left(-\frac{\beta}{P}\sum\nolimits_I\frac{\hat{P}_I^2}{2M_I}\right)\left|R_{s-1}\right\rangle$$

$$\times\exp\left(-\frac{\beta}{P}\frac{E_0(R_s)+E_0(R_{s-1})}{2}\right)\delta_{i_s,0}\delta_{i_{s-1},0}$$

from the adiabatic sense. The overlap appearing above can be approximated by using Taylor expansion as

$$S_{s,s-1} \equiv \langle\psi_0(R_s)|\psi_0(R_{s-1})\rangle = \int dr\psi_0^*(r;R_s)\psi_0(r;R_{s-1})$$

$$= 1+\frac{1}{2}\sum_{I,J}\left(R_{I,s-1},R_{I,s}\right)\left(R_{J,s-1},R_{J,s}\right)\int dr\psi_0^*(r;R_s)\nabla_{I,s}\nabla_{I,s-1}\psi_0(r;R_{s-1})$$

where we have assumed that the wave function is real, so that we can apply

$$\int dr\psi_0^*(r;R)\nabla_I\psi_0(r;R) = 0.$$

Since the derivative terms are small, we can reasonably assume that the overlap is small. Then

$$\rho(s,s-1;\tau) \simeq \exp\left(-\frac{\beta}{P}\sum_I\frac{M_I}{2}\left(\frac{\sqrt{P}}{\beta\hbar}\right)^2\left(R_{I,s}-R_{I,s-1}\right)^2\right)$$

$$\times \exp\left(-\frac{\beta}{P}\frac{E_0(R_s)+E_0(R_{s-1})}{2}\right)\delta_{i_s,0}\delta_{i_{s-1},0}$$

Therefore, we have

$$Z=\prod_I\left[\left(\frac{M_I P}{2\pi\beta\hbar}\right)^{\frac{3P}{2}}\right]\int dR_1\cdots dR_P \exp\left(-\beta\sum_s\sum_I\frac{M_I}{2}\left(\frac{\sqrt{P}}{\beta\hbar}\right)^2\left(R_{I,s}-R_{I,s-1}\right)^2+\frac{1}{P}E_0(R_s)\right)$$

This has the same form as the partition function of classical systems having $N\times P$ particles interacting via

$$\mathrm{V_{eff}}=\sum_s\sum_I\frac{M_I}{2}\left(\frac{\sqrt{P}}{\beta\hbar}\right)^2\left(R_{I,s}-R_{I,s-1}\right)^2+\frac{1}{P}E_0(R_s)$$

This means that, if we perform a molecular dynamics (MD) simulation using NP particles under a constant temperature T, we get canonical ensemble of N quantum particles. So, the problem is then how to do the DFT MD simulation. In fact, the method is well established. The quantum simulation can be done conveniently using, for example, PIMD developed by Dr. Shiga.

http://ccse.jaea.go.jp/ja/download/pimd/index.jp.html

Linear response within classical statistical physics

Here I discuss a theory of density correlation for a classical many-body stem to be compared with DFT. The method is based on the standard statistical physics of a grand canonical ensemble. We start from the Ornstein Zernike (OZ) equation. For detail, please read the article written by Prof. Sato, (http://j-molsci.jp/archives/AC0004.pdf).

We now see how the correlation factors are described in a classical system

(a) fluctuation and correlation

Let us define the density operator

$$\delta n(\vec{r})=\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)-n_0,$$

where n_0 is the density averaged over the whole system. The average of $\delta n(\vec{r})$ over the ensemble is zero, or

$$\langle\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)\rangle=n_0.$$

The density fluctuation can be written as

$$\langle \delta n(\vec{r})\delta n(\vec{r}')\rangle = \langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) \sum_{j=1}^{N} \delta\big(\vec{r}'-\vec{r}_j\big)\rangle - 2n_0 \langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\rangle + n_0^2$$

$$= \langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\,\delta(\vec{r}'-\vec{r}_i)\rangle + \langle \sum_{i,j=1,i\neq j}^{N} \delta(\vec{r}-\vec{r}_i)\,\delta\big(\vec{r}'-\vec{r}_j\big)\rangle - n_0^2$$

$$= n_0\delta(\vec{r}-\vec{r}') + n_0^2 g(\vec{r},\vec{r}') - n_0^2 = n_0\delta(\vec{r}-\vec{r}') + n_0^2 h(\vec{r},\vec{r}')$$

where g is the pair correlation function

$$g(\vec{r},\vec{r}') \equiv \langle \sum_{i,j=1,i\neq j}^{N} \delta(\vec{r}-\vec{r}_i)\,\delta\big(\vec{r}'-\vec{r}_j\big)\rangle$$

and h is called as the total correlation function (two-body density matrix over square of the particle density)

$$h(\vec{r},\vec{r}') \equiv g(\vec{r},\vec{r}') - 1.$$

Note that similar quantities have been discussed above although the naming is somewhat different. ($n_0^2 h(\vec{r},\vec{r}') \leftrightarrow n_2(\boldsymbol{r},\boldsymbol{r}')$)

To relate the correlation with the response function, it is convenient to introduce a functional derivative scheme. In the first step, let us relate the correlation with the partition function.

(b) grand partition function and grand distribution function

Then, we focus on the grand partition function. For a system described by the Hamiltonian,

$$H = \sum_{i}^{N} \frac{1}{2m_i}\vec{p}_i^{\,2} + U_N(1,\cdots,N),$$

the partition function is written as, using the thermal de Broglie wave length $\Lambda = h/\sqrt{2\pi m k_B T}$,

$$\Xi = \sum_{N=0}^{\infty} \iiint \frac{1}{\Lambda^{3N} N!} \exp[-\beta(U_N(1,\cdots,N)-\mu)]\, d(1\ldots N)$$
$$= \sum_{N=0}^{\infty} \iiint \frac{z^N}{N!} \exp[-\beta U_N(1,\cdots,N)]\, d(1\ldots N),$$

where z is the activity

$$z = \Lambda^{-3}\exp(\beta\mu),$$

and the m-particle distribution function (classical analogue of the m-body density matrix) is given as

$$n^{(m)}(1,\cdots,m)=\frac{1}{\Xi}\sum_{N=0}^{\infty}\iiint d(1\ldots N)\frac{z^N}{N!}\exp[-\beta U_N(1,\cdots,N)]$$
$$\times\sum_{i}\sum_{j\neq i}\cdots\sum_{k\neq i,j,\cdots}\delta(1-\vec{r}_i)\delta\left(2-\vec{r}_j\right)\cdots\delta(n-\vec{r}_k).$$

This can be rewritten as a sum of multiples of the canonical partition function Z_N and the canonical distribution function $n_N^{(m)}$

$$n^{(m)}(1,\cdots,m)=\frac{1}{\Xi}\sum_{N=0}^{\infty}\frac{z^N}{N!}Z_N n_N^{(m)}(1,\cdots,m)$$

Note that

$$\iiint d(1\ldots N)n_N^{(m)}(1,\cdots,m)=\frac{N!}{(N-m)!}.$$

Now that the correlation functions are given in terms of the partition function, let us consider the functional derivative method.

(c) Functional derivative

When the potential energy consists of the external potential and the rest as

$$U_N(1,\cdots,N)=\sum_{i=1}^{N}V(i)+U'_N(1,\cdots,N)$$

the grand partition function can be written using generalized activity

$$z(\vec{r})=z\exp[-\beta V(\vec{r})]$$
$$z(i)=z\exp[-\beta V(\vec{r}_i)]$$

as

$$\Xi=\sum_{N=0}^{\infty}\iiint\frac{1}{N!}\left(\prod_{i=1}^{N}z(i)\right)\exp\left[-\beta\left(U'_N(1,\cdots,N)\right)\right]d(1\ldots N).$$

When this is differentiated by $z(\vec{r})$, we get

$$\frac{\delta\Xi}{\delta z(\vec{r})}=\sum_{N=0}^{\infty}\iiint\frac{1}{N!}\sum_{i}\frac{\delta z(i)}{\delta z(\vec{r})}\left(\prod_{j=1,j\neq i}^{N}z(j)\right)\exp\left[-\beta\left(U'_N(1,\cdots,N)\right)\right]d(1\ldots N)$$

$$=\sum_{N=0}^{\infty}\iiint\frac{1}{N!}\sum_{i}\delta(\vec{r}_i-\vec{r})\left(\prod_{j=1,j\neq i}^{N}z(j)\right)\exp[-\beta(U'_N(1,\cdots,N))]d(1\ldots N)$$

$$=\sum_{N=0}^{\infty}\iiint\frac{1}{(N-1)!}\left(\prod_{j=2}^{N}z(j)\right)\exp\left[-\beta\left(U'_N(\vec{r},2,\cdots,N)\right)\right]d(2\ldots N).$$

Comparing with the above equations for the distribution functions, we can show

$$n^{(1)}(\vec{r}) = \frac{z(\vec{r})}{\Xi}\frac{\delta \Xi}{\delta z(\vec{r})} = \frac{\delta \ln \Xi}{\delta \ln z(\vec{r})}$$

$$n^{(2)}(\vec{r},\vec{r}') = z(\vec{r}')\frac{\delta n^{(1)}(\vec{r})}{\delta z(\vec{r}')} = \frac{\delta n^{(1)}(\vec{r})}{\delta \ln z(\vec{r}')}.$$

Note that $\delta \ln z(\vec{r}) = -\beta \delta V(\vec{r})$, so that

$$n^{(2)}(\vec{r},\vec{r}') = -k_B T \frac{\delta n^{(1)}(\vec{r})}{\delta V(\vec{r}')}.$$

This is a fluctuation dissipation theorem in the sense that the two-body density is related to the response of the density to the local potential.

Let us then consider inverse of the response function

$$-\beta \frac{\delta n^{(1)}(\vec{r})}{\delta V(\vec{r}')}.$$

This should be the inverse of the non-interacting response function minus the interaction kernel. When no interaction exists,

$$n_0^{(1)}(\vec{r}) = \exp[-\beta V(\vec{r})],$$

so that

$$\chi^{(0)-1}(\vec{r},\vec{r}') = -\beta \frac{\delta V(\vec{r})}{\delta n^{(1)}(\vec{r}')} = \frac{\delta(\vec{r}-\vec{r}')}{n_0^{(1)}(\vec{r})}.$$

Deviation from this is the result of the interaction, which will be denoted by $K(\vec{r},\vec{r}')$ as

$$\chi^{-1}(\vec{r},\vec{r}') \equiv \frac{\delta \ln z(\vec{r})}{\delta n^{(1)}(\vec{r}')} = -\beta \frac{\delta V(\vec{r})}{\delta n^{(1)}(\vec{r}')} \equiv \frac{\delta(\vec{r}-\vec{r}')}{n^{(1)}(\vec{r})} - K(\vec{r},\vec{r}').$$

When we use the chain rule

$$\int \frac{\delta n^{(1)}(\vec{r})}{\delta \ln z(\vec{r}'')}\frac{\delta \ln z(\vec{r}'')}{\delta n^{(1)}(\vec{r}')} = \delta(\vec{r}-\vec{r}')$$

we get

$$\int \left(n(\vec{r})\delta(\vec{r}-\vec{r}'') + n(\vec{r})h(\vec{r},\vec{r}'')n(\vec{r}'')\right)\left(\frac{\delta(\vec{r}''-\vec{r}')}{n(\vec{r}'')} - K(\vec{r}'',\vec{r}')\right)d\vec{r}'' = \delta(\vec{r}-\vec{r}'),$$

and further

$$n(\vec{r})h(\vec{r},\vec{r}') - n(\vec{r})K(\vec{r},\vec{r}') - n(\vec{r})\int h(\vec{r},\vec{r}'')n(\vec{r}'')K(\vec{r}'',\vec{r}')\,d\vec{r}'' = 0$$

$$h(\vec{r},\vec{r}') - K(\vec{r},\vec{r}') - \int h(\vec{r},\vec{r}'')n(\vec{r}'')K(\vec{r}'',\vec{r}')\,d\vec{r}'' = 0$$

which is the OZ equation to relate the inverse of the response function with the density correlation via a Dyson-like equation. Note that this derivation shows that OZ does not require a pair-wise interaction. When the interaction kernel K is given as a functional of the density $n(\boldsymbol{r})$ using the DFT for classical particles, the correlation h is determined. In the classical DFT, there are known approximate and explicit relation of K and h when the particles are interacting via a two-body force. The relation is called as a closure and the famous ones are the hypernetted chain closure and the Percus-Yevic closure.

Maximally localized Wannier orbitals

In solid state physics, Wannier orbitals are constructed from the Bloch orbitals by taking a "Fourier transformation". Wannier orbital is localized spatially with the decay rate depending on the electronic structure; it decays exponentially for insulators and polynomially for metals. The decay rate can be enhanced by adding different bands to the transformation. When this is done maximally, the orbitals are localized in atomic scale and can be taken as atomic orbitals under the crystalline environment. The resulting orbitals can be conveniently used as a basis of the strongly correlated electron models. In addition, it has a peculiar property surprisingly suitable for the study of ferroelectrics.

Formulation

We begin by defining the Wannier orbitals taking the phase factor φ explicitly taken into account.

$$|R_n\rangle = \frac{\Omega}{(2\pi)^3} \int_{BZ} |\psi_{nk}\rangle e^{i\varphi(k)-ikR} dk$$

Here, $\psi_{nk}(r)$ is the Bloch orbital,

$$\psi_{nk}(r) = u_{nk}(r)e^{ikr}: \qquad u_{nk}(r) = u_{nk}(r+R),$$

R is the lattice vector and $\varphi(k)$ is the phase factor that is periodic in BZ; $\varphi(k) = \varphi(k+G)$ for reciprocal lattice vectors G. We can localize the orbitals more by including a unitary transformation among bands:

$$|R_n\rangle = \frac{\Omega}{(2\pi)^3} \int_{BZ} \sum_m U_{mn}^k \, |\psi_{mk}\rangle e^{i\varphi(k)-ikR} dk$$

The transformation matrix U can be determined by minimizing a variance

$$L = \sum_n (\langle 0_n | r^2 | 0_n\rangle - \langle 0_n | r | 0_n\rangle^2)$$

One can show that the matrix elements can be written using the periodic part of the Bloch function and derivatives in the reciprocal space.

$$\langle R_n | r | 0_m\rangle = i \frac{\Omega}{(2\pi)^3} \int_{BZ} \langle u_{nk} | \nabla_k | u_{mk}\rangle e^{ikR} dk$$

$$\langle R_n | r^2 | 0_m \rangle = i \frac{\Omega}{(2\pi)^3} \int_{BZ} \langle u_{nk} | \nabla_k^2 | u_{mk} \rangle e^{ikR} dk$$

The derivatives are in practice estimated using the finite mesh points spanning the Brillouine zone; this is the computational physics. In this case, we approximate the derivative by a finite difference as

$$\nabla f(k) = \sum_b w_b b[f(k+b) - f(k)]$$

where b's are vectors chosen so that k and $k+b$ are neighboring mesh points. Similarly,

$$\nabla^2 f(k) = \sum_b w_b b[f(k+b) - f(k)]^2$$

This indicates that $\langle u_{nk} | \nabla_k | u_{mk} \rangle$ is approximated using overlaps of the form $\langle u_{nk} | u_{mk+b} \rangle$. It was shown that

$$\langle 0_n | r | 0_n \rangle = -\frac{1}{N} \sum_{k,b} w_b \, b \, \mathrm{Im}(\ln\langle u_{nk} | u_{nk+b} \rangle): \qquad \text{Wannier center}$$

$$\langle 0_n | r^2 | 0_n \rangle = -\frac{1}{N} \sum_{k,b} w_b \{1 - |\langle u_{nk} | u_{nk+b} \rangle|^2 + |\mathrm{Im}(\ln\langle u_{nk} | u_{nk+b} \rangle)|^2\}$$

hold. Therefore, the overlaps, $\mathrm{M}_{\mathrm{nm}}^{(k,b)} \equiv \langle u_{nk} | u_{mk+b} \rangle$, plays the central role in calculating the localized Wannier orbitals.

Modern theory of polarization

1. Motivation: Intuitive definition of polarization will be

$$\boldsymbol{P} = \frac{1}{\Omega} \int_{cell} dr \boldsymbol{r} \rho(\boldsymbol{r}),$$

where Ω is the volume of the cell and $\rho(r)$ is the charge density, but this is ambiguous for solids. The result depends on how we take the origin and also how we take the unit cell. This is the well-known problem of the polarization. You may consider that the real materials are finite, so that the polarization should be well-defined after integrating over the whole sample. In that case, the integration can be transformed to the surface integration using the Green's theorem. Thus, the theory requires argument of the surface. But, there is a way to define the polarization using the unit cell information only.

2. New approach: One can solve the problem of the ill-defined "crystalline polarization" by considering "flow of charge" associated with displacement of ions. Phenomenologically, the polarization occurs associated with the ionic displacement, such that the polarization P is zero at an initial configuration of ions but is nonzero at a displaced configuration. This fact makes it possible to define the polarization by connecting the initial unpolarized state to the final polarized state continuously and integrate the associated flow of charge as

$$P = \int dt \frac{1}{\Omega} \int_{cell} dr \boldsymbol{j}(\boldsymbol{r}, t).$$

This “adiabatic” definition has made it possible to modernize the theory of polarization.

2.1 (DFPT formulation) Before introducing the modern theory, let us apply the DFPT explaining associated problems. To make the polarization to occur, we apply electric field with large wave length; because of the ill-defined nature as explained above, the wave length is let to be finite and will be extrapolated to infinity after the calculation. Because of the electric field, the atoms will be displaced in proportional to the field strength thereby generating a polarization $P_0 = Z_\tau R$. The nuclear charge Z_τ can be defined alternatively as the derivative of the polarization with respect to the atomic displacement δR. This can be also described as the second derivative of the total energy with respect to the electric field and the atomic displacement $\frac{\partial^2 E_{\text{tot}}}{\partial E \partial R}$. The electron density will also be changed by the electric filed by $\frac{\partial \rho}{\partial E}\delta E + \frac{\partial \rho}{\partial R}\delta R + \frac{1}{2}\frac{\partial^2 \rho}{\partial E \partial R}\delta E \delta R + \cdots$: Because the first order changes are zero, the second order is important. Since the uniform electric field is also ill-defined, we practically apply the field of finite wave length and then extrapolated to infinity after calculation. From the second derivative modifies the value of *Z*, as $Z\tau + Z_{\text{eff}}$, which is called Born effective charge. This is a DFPT approach to the Born effective charge. The modern approach is different.

3. Formulation: Let us introduce a parameter λ connecting the unpolarized and the polarized states; you may regard λ as a parameter for the displacement. By applying a first-order perturbation theory, change of the wave function can be written as

$$|\delta\psi_{nk}\rangle = -i\hbar\delta\lambda \sum_{m \neq n} \frac{\langle\psi_{mk}|\partial_\lambda|\psi_{nl}\rangle}{E_{nk} - E_{mk}} |\psi_{mk}\rangle$$

Corresponding current is obtained by calculating the expectation value of the current operator as,

$$j_n = \frac{dP_n}{dt} = \frac{i\hbar e\dot{\lambda}}{(2\pi)^3} \sum_{m \neq n} \int dk \frac{\langle\psi_{nk}|p|\psi_{ml}\rangle\langle\psi_{mk}|\partial_\lambda|\psi_{nl}\rangle}{E_{nk} - E_{mk}} + c.c.$$

This can rewritten using the periodic part of the Bloch wave function. The result is

$$\frac{dP_n}{dt} = \frac{ie\dot{\lambda}}{(2\pi)^3} \int dk \langle\nabla_k u_{nk}|\partial_\lambda u_{nk}\rangle + c.c.$$

This is appealing in that the contribution from the unoccupied states disappears and that the derivative with respect to k is conveniently accessed by the maximally localized Wannier orbital method.

When summing over all the occupied states n and integration over t (to connect the initial and final states) we finally arrive at

$$P(\lambda) = \frac{e}{(2\pi)^3} \mathrm{Im} \sum_n \int dk \langle u_{nk} | \nabla_k | u_{nk} \rangle$$

$$\Delta P = P(1) - P(0) = P(1)$$

This is equivalent to the quantity appearing in the Berry phase theory and thus we will regard $i\langle u_{nk} | \nabla_k | u_{nk} \rangle$ as a Berry connection or gauge potential. Note that this is the electronic contribution to the polarization. We need to add the ionic contribution

$$P_{\mathrm{ion}} = \frac{e}{\Omega} \sum_\tau Z_\tau R_\tau,$$

as

$$P = \frac{e}{(2\pi)^3} \mathrm{Im} \sum_n \int dk \langle u_{nk} | \nabla_k | u_{nk} \rangle + \frac{e}{\Omega} \sum_\tau Z_\tau R_\tau$$

This way we arrive at this very useful formula.

4. Quantum of polarization: Suppose we are integrating over a path within a one-dimensional Brillouine zone;

$$P_n = \frac{e}{2\pi} \phi_n = \frac{e}{2\pi} \mathrm{Im} \int_{-\pi/L}^{\pi/L} dk \langle u_{nk} | \partial_k | u_{nk} \rangle$$

In this case, the initial and final points are equivalent because of the periodicity. So, the above integration path corresponds to a closed loop.

The phase of the wave function can be taken arbitrarily like

$$\tilde{u}_{nk} = e^{-i\beta(k)} u_{nk}$$

except that the difference at the boundary $\beta(\pi/L) - \beta(-\pi/L)$ is a multiple of 2π. When the polarization is calculated using this new wave function, we get

$$\tilde{\phi}_n = \phi_n + 2\pi m: \qquad m \in \text{Integer}$$

indicating that the polarization can be defined within the modulo of e. In other words, we cannot definite uniquely the crystalline polarization, which may be understood as different paths can be used to connect the equivalent points in the Brillouine zone.

When this discussion is extended to a 3D system, it can be shown that the polarization is well defined within the modulo of

$$eR/\Omega$$

where R is a lattice vector

$$R = \sum_j m_j R_j.$$

Please see a literature on modern theory of polarization for the proof.

The polarization can be rewritten using the relation $r = -\frac{i\partial}{\partial k}$, as the real part of

$$P_n = -e \int_{-\frac{\pi}{L}}^{\frac{\pi}{L}} \frac{dk}{2\pi} \langle u_{nk} | -i\partial_k | u_{nk} \rangle = -e \int_{-\pi/L}^{\pi/L} \frac{dk}{2\pi} \langle u_{nk} | r | u_{nk} \rangle$$

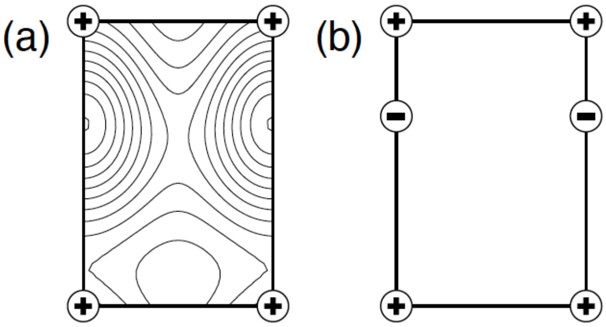
5. Wannier center: We have learned that the Wannier orbitals are

$$w_n(r-R)=\Omega\int_{BZ}\frac{d^3k}{(2\pi)^3}e^{-ikR}\psi_{nk}(r)=\Omega\int_{BZ}\frac{d^3k}{(2\pi)^3}e^{ik(r-R)}u_{nk}(r).$$

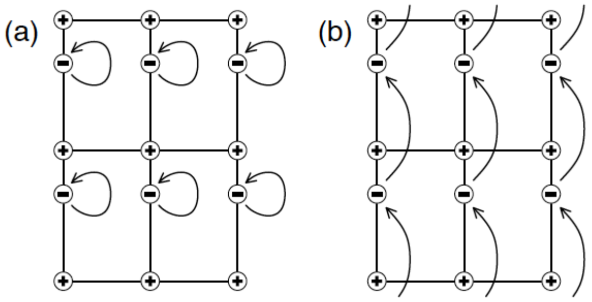
Then, it is possible to show that the polarization can be described by the position of the Wannier center (after adding the contribution from the nuclear charge)

$$P_n=\frac{e}{\Omega}(r_{nR}-R)=\frac{e}{\Omega}(\langle w_{nR}|r|w_{nR}\rangle-R).$$

Note that the Wannier center represents the spatially distributed charge density as a point charge (see figure). We can thus regard the polarization effectively as the charge assigned to the Wannier center. Note that the calculation can be done efficiently when using the most localized Wannier orbitals, instead of the standard one shown here, but that formulation is skipped here.



There are various ways to relate it to the flow of charge differently like



This difference corresponds to the existence of modulus.

Now that the formulation has been given, we now follow the tutorial done by QE community in India. Do the calculation and see what will result. After that, try to explain in your words what you did there.

Density functional perturbation theory

(http://iffwww.iff.kfa-juelich.de/~wortmann/IFF-Springschool45/C2.pdf)

Here we study the perturbation theory within DFT, namely DFPT. DFPT is different from the perturbation theory of noninteracting systems in that the density response should also be taken into account. I will introduce DFPT in relation to the polarization of materials.

1. Sternheimer equation for noninteracting systems

The first-order change in the wave function $\psi_i^{(1)}$ can be obtained by solving the Sternheimer equation

$$\left(H^{(0)}-\varepsilon^{(0)}\right)\left|\psi_i^{(1)}\right\rangle = -\left(H^{(1)}-\varepsilon^{(1)}\right)\left|\psi_i^{(0)}\right\rangle$$

where H^0 and ε^0 are unperturbed ones and $H^{(1)}$ and $\varepsilon^{(1)}$ are the perturbed ones and

$$\varepsilon^{(1)} = \left\langle\psi_i^{(0)}\middle|H^{(1)}\middle|\psi_i^{(0)}\right\rangle.$$

This equation is solved by superimposing the unperturbed states as

$$\left|\psi_i^{(1)}\right\rangle = \sum_j c_{ij}^{(1)}\left|\psi_j^{(0)}\right\rangle = \sum_{j\in I} c_{ij}^{(1)}\left|\psi_j^{(0)}\right\rangle + \sum_{j\in I^\perp} c_{ij}^{(1)}\left|\psi_j^{(0)}\right\rangle$$

where I and $I^\perp$ are states degenerate to $\psi_i^{(0)}$ and other states, respectively. By this definition,

$$\left(H^{(0)}-\varepsilon_i^{(0)}\right)\left|\psi_i^{(1)}\right\rangle = \sum_{j\in I^\perp} c_{ij}^{(1)}\left(\varepsilon_j^{(0)}-\varepsilon_i^{(0)}\right)\left|\psi_j^{(0)}\right\rangle.$$

Therefore,

$$c_{ij}^{(1)} = -\frac{\left\langle\psi_j^{(0)}\middle|H^{(1)}\middle|\psi_i^{(0)}\right\rangle}{\varepsilon_j^{(0)}-\varepsilon_i^{(0)}} \quad \text{for } j \in I^\perp.$$

Using the gauge degrees of freedom to set $c_{ij}^{(1)} = 0$ for $j \in I$. Therefore,

$$\left|\psi_i^{(1)}\right\rangle = -\sum_{j\in I^\perp}\left|\psi_j^{(0)}\right\rangle\frac{\left\langle\psi_j^{(0)}\middle|H^{(1)}\middle|\psi_i^{(0)}\right\rangle}{\varepsilon_j^{(0)}-\varepsilon_i^{(0)}}.$$

This can be alternatively written as

$$P_I^\perp\left(H^{(0)}-\varepsilon_i^{(0)}\right)P_I^\perp\left|\psi_i^{(1)}\right\rangle = -P_I^\perp H^{(1)}\left|\psi_i^{(0)}\right\rangle \quad \text{with } P_I^\perp = \sum_{j\in I^\perp}\left|\psi_j^{(0)}\right\rangle\left\langle\psi_j^{(0)}\right|$$

or

$$P_I^\perp\left|\psi_i^{(1)}\right\rangle = G_{I^\perp}\left(\varepsilon_i^0\right)H^{(1)}\left|\psi_i^0\right\rangle \quad \text{with } G_{I^\perp}(\varepsilon) = \left[P_I^\perp\left(\varepsilon - H^{(0)}\right)P_I^\perp\right]^{-1}.$$

2. DFT

In DFT, one has to take the density variation into account. The first-order change in the energy is

$$\frac{d}{d\lambda}\sum_i\langle\psi_i|T+V_{\mathrm{ext}}+V_{\mathrm{H}}+V_{\mathrm{xc}}|\psi_i\rangle = \left\langle\psi_i^{(0)}\middle|\left(T+V_{\mathrm{ext}}\right)^{(1)}\middle|\psi_i^{(0)}\right\rangle + \frac{d}{d\lambda}E_{\mathrm{Hxc}}\left[\rho^{(0)}\right].$$

The second order change is

$$\left\langle\psi_i^{(0)}\middle|(T+V_{\text{ext}})^{(2)}\middle|\psi_i^{(0)}\right\rangle+\left\langle\psi_i^{(1)}\middle|(T+V_{\text{ext}})^{(1)}\middle|\psi_i^{(0)}\right\rangle+\left\langle\psi_i^{(0)}\middle|(T+V_{\text{ext}})^{(1)}\middle|\psi_i^{(1)}\right\rangle$$
$$+\left\langle\psi_i^{(1)}\middle|(T+V_{\text{ext}})^{(0)}\middle|\psi_i^{(1)}\right\rangle$$
$$+\frac{1}{2}\iint\frac{\delta^2E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\delta\rho(r)\delta\rho(r')}\rho^{(1)}(r)\rho^{(1)}(r')drdr'+\int\frac{d}{d\lambda}\left(\frac{\delta E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\delta\rho(r)}\right)\rho^{(1)}(r)dr$$
$$+\frac{1}{2}\frac{d^2}{d\lambda^2}E_{\text{Hxc}}\left[\rho^{(0)}\right],$$

with

$$\rho^{(1)}(r)=\sum_i\psi_i^{(1)*}(r)\psi_i^{(0)}(r)+\psi_i^{(0)*}(r)\psi_i^{(1)}(r).$$

The perturbed Kohn-Sham orbitals $\psi_i^{(1)}$ are obtained by solving the Sternheimer equation:

$$\left(H^{(0)}-\varepsilon_i^{(0)}\right)\left|\psi_i^{(1)}\right\rangle=-\left(H^{(1)}-\varepsilon_i^{(1)}\right)\left|\psi_i^{(0)}\right\rangle,$$

with

$$H^{(1)}=(T+V_{\text{ext}})^{(1)}+\int\frac{\delta^2E_{\text{Hxc}}\left[\rho^{(0)}\right]}{\delta\rho(r)\delta\rho(r')}\rho^{(1)}(r')dr'$$

and

$$\varepsilon_i^{(1)}=\left\langle\psi_i^{(0)}\middle|H^{(1)}\middle|\psi_i^{(0)}\right\rangle.$$

3. DFPT for polarization

Let us study the polarization, which can be characterized by change in the polarization P_β caused by a uniform displacement of an atom κ in the direction $R_{\kappa\alpha}$: here uniform means that the atom in a cell is displaced together with its periodic images. The relevant quantity is the Born effective charge defined by

$$Z_{\kappa,\beta\alpha}^*=\Omega\frac{\partial P_\beta}{\partial R_{\kappa\alpha}}.$$

Since the total energy can be described as

$$E[\rho]-\Omega\mathrm{P}\cdot\mathcal{E}$$

under the electric field $\mathcal{E}$ induced by the polarization,

$$P_\beta=-\frac{1}{\Omega}\frac{\partial E[\rho]}{\partial\mathcal{E}_\beta}.$$

Therefore,

$$Z^{*}_{\kappa,\beta\alpha} = -\frac{\partial^{2} E[\rho]}{\partial R_{\kappa\alpha}\partial \mathcal{E}_{\beta}}.$$

This can be calculated by applying the DFPT. Since the E_{Hxc} has not dependence on the atomic displacement and electric field, $T + V_{\mathrm{ext}}$ does not depend on the electric field, and the kinetic energy operator is not affected by a uniform atomic displacement, the equation is simplified as

$$\frac{\partial^{2} E[\rho]}{\partial R_{\kappa\alpha}\partial \mathcal{E}_{\beta}} = \left\langle \psi_i^{(\mathcal{E}_\beta)} \middle| (V_{\mathrm{ext}})^{(R_{\kappa\alpha})} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \middle| (V_{\mathrm{ext}})^{(R_{\kappa\alpha})} \middle| \psi_i^{(\mathcal{E}_\beta)} \right\rangle + 2 \left\langle \psi_i^{(R_{\kappa\alpha})} \middle| (T + V_{\mathrm{ext}})^{(0)} \middle| \psi_i^{(\mathcal{E}_\beta)} \right\rangle$$
$$+ \iint \frac{\delta^{2} E_{\mathrm{Hxc}}\left[\rho^{(0)}\right]}{\delta\rho(r)\delta\rho(r')} \rho^{(R_{\kappa\alpha})}(r) \rho^{(\mathcal{E}_\beta)}(r') dr dr',$$

So, we need to solve the Sternheimer equation twice to get $\psi_i^{(R_{\kappa\alpha})}$ and $\psi_i^{(\mathcal{E}_\beta)}$, corresponding to change in the Kohn-Sham orbitals with respect to the atomic displacement and the generation of the electric field.

About quantum espresso

Now let us use the environment

https://www.materialscloud.org/work/quantum-mobile

which will install a virtual machine (Virtual Box 5.2.8 + Ubuntu 16.04.4LTS) on which you can run quantum espresso (v6.2.1) and wannier90 (2.1).

<First assignment: transfer of the benzene >

Change your directory to wannier90-2.1 (depending on the version you installed) and then to examples/example12. Then you will find input files for the calculation of benzene.

First, do an SCF calculation: In the SCF calculation, you get the effective Kohn-Sham potential, electron density and KS orbitals.

```
pw.x < benzene.scf > scf.out
```

Second, run wannier90 to generate a list of the required overlaps (written into the benzene.nnkp file).

```
wannier90.x -pp benzene
```

Third, run pw2wannier90 to compute the overlap between Bloch states and the projections for the starting guess (written in the benzene.mmn and benzene.amn files).

```
pw2wannier90.x < benzene.pw2wan > pw2wan.out
```

Finally, run wannier90 to compute the MLWFs.

```
wannier90.x benzene
```

Do this again by adding the lines to the benzene.win

```
    restart = plot
    wannier_plot = true
    wannier_plot_format = cube
    wannier_plot_list = 2-4
```

Then you have files for the second to fourth MLWFs. By changing the digits, you can draw all the orbitals.

1. Use xcrysden to draw all the MLWFs.

Do the same thing after you have inserted a line at the end of benzene.win

```
write_hr = true
```

Then you will get benzene_hr.dat

Focus on the third to fifth columns, say a, b, H. It indicates the transfer integral between the atoms a and b is H.

2. Show the value of transfer on a picture describing the structure of benzene. You need to show only the largest ones, for example, only those whose magnitude is larger than 1 eV.

3. Describe scientific significance of the results.

<Second assignment: Born effective charge of Pb in $PbTiO_3$ >

Following the example04 of the quantum espresso, calculate the Born-effective charge of Pb. Explain briefly procedures for the calculation, important parameters in the input file, result of the calculation. For this, use the ball and stick model obtained using, for example, xcrysden. Also, show scientific significance of the result.