TCC Electronic Structure Module
L7: Density Functional Theory

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Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

L1 Exact and inexact wavefunctions

L2 Hartree–Fock theory

L3 Configuration Interaction theory

L4 Møller–Plesset perturbation theory

L5 Coupled-cluster theory

L6 Properties and excited states

L7 Density Functional Theory

L8 Density Functional Approximations

Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

1 Introduction

Density Functional Theory (DFT) is very different approach to computing molecular energies and properties. It has an excellent accuracy-to-cost ratio and can be applied equally to molecules, solids (both conducting and insulating) and interfaces and has found widespread use in chemistry, biology, physics and materials sciences. The formal aspects of the theory are a substantial departure from wavefunction theory, but the computer implementation is very similar to Hartree–Fock Theory.

Further reading: Excellent lecture notes by Julien Toulouse, where much of these notes are drawn from.
http://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_dft.pdf

2 Conceptual Framework of DFT

In quantum mechanics, the wavefunction fully defines the state of the system. It evolves through time according to Schrödinger's equation and can be used to obtain any properties of the system. Stationary states with properties that do not vary with time have wavefunctions that satisfy the time-independent Schrödinger equation. A central objective is to establish methods for computing the ground state energy. To that end, we write the energy as a functional of a wavefunction and use the variational principle to locate the ground state:

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min_{\Psi} E[\Psi] \tag{1}$$

where the search is over all n-electron (antisymmetric) wavefunctions and we have defined the energy functional $E[\Psi]$ as the energy expectation value. In Density Functional Theory, this ground state search is recast in terms of the electron density without reference to the wavefunction at all. It is not obvious that this is possible.

Reminder: the definition of the electron density is

$$\rho(\mathbf{r}) = n \int d\sigma d\mathbf{x}_2 \dots d\mathbf{x}_n \Psi^*(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_n) \Psi(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_n) \tag{2}$$

Some DFT nomenclature: The Hamiltonian contains a universal n-electron part and a molecule dependent part $v(\mathbf{r})$

$$\hat{F} = \hat{T} + \hat{V}_{ee} = \sum_{i}^{n} -\frac{1}{2}\nabla_i^2 + \sum_{i<j}^{n} \frac{1}{r_{ij}} \tag{3}$$

$$\hat{V} = v(\mathbf{r}) = -\sum_{iI}^{nN} \frac{Z_I}{r_{iI}} \tag{4}$$

2.1 The Hohenberg-Kohn Theorems

DFT is founded on two theorems by Hohenberg and Kohn. The first establishes that it is possible to formally express both the ground state wavefunction and the ground state energy for a given $v(\mathbf{r})$ as (very complicated) functionals of the ground state density, $\Psi[\rho]$ and $E[\rho]$. The second establishes that it is formally possible to search over trial densities variationally to locate both the exact ground state density and the exact ground state energy.

2.1.1 HK-1

If you know the ground state density, then you also know the potential $v(\mathbf{r})$ up to a constant.
We say that the ground state density determines the potential: $\rho(\mathbf{r}) \longrightarrow v(\mathbf{r}) + \text{const}$

Since $\rho(\mathbf{r})$ also determines the number of electrons, the consequence is that the ground state density fully determines the Hamiltonian and, by extension, fully determines the ground state wavefunction and the ground state energy. $\rho \longrightarrow \hat{H} \longrightarrow E, \Psi$

The proof is a two step proof by contradiction. Consider two local potentials differing by more than an additive constant: $v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + \text{const}$. We have two Hamiltonians:

$\hat{H}_1 = \hat{F} + \hat{V}_1$ with a ground state $\hat{H}_1|\Psi_1\rangle = E_1|\Psi_1\rangle$ and ground-state density $\rho_1(\mathbf{r})$

$\hat{H}_2 = \hat{F} + \hat{V}_2$ with a ground state $\hat{H}_2|\Psi_2\rangle = E_2|\Psi_2\rangle$ and ground-state density $\rho_2(\mathbf{r})$

We first show that $\Psi_1 \neq \Psi_2$. Let us assume that $\Psi_1 = \Psi_2 = \Psi$ and consider the consequences. We then have

$$(\hat{H}_1 - \hat{H}_2)|\Psi\rangle = (\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle \tag{5}$$

Writing this in position representation

$$\sum_i^n [v_1(\mathbf{r}_i) - v_2(\mathbf{r}_i)]\Psi(\mathbf{x}_1 \dots \mathbf{x}_n) = (E_1 - E_2)\Psi(\mathbf{x}_1 \dots \mathbf{x}_n) \tag{6}$$

makes it clear that the only way for this to be true without $\Psi = 0$ is if $v_1(\mathbf{r}) = v_2(\mathbf{r}) + \text{const}$, in contradiction of our premise. Therefore two local potentials differing by more than an additive constant cannot share the same ground-state wave function.

We now show that $\rho_1 \neq \rho_2$. Let us assume that $\rho_1 = \rho_2 = \rho$. By the variational principle we have

$$\begin{aligned} E_1 = \langle\Psi_1|\hat{H}_1|\Psi_1\rangle &< \langle\Psi_2|\hat{H}_1|\Psi_2\rangle & (7)\\ &< \langle\Psi_2|\hat{H}_2 + \hat{V}_1 - \hat{V}_2|\Psi_2\rangle & (8)\\ &< E_2 + \int d\mathbf{r}\,[v_1(\mathbf{r}) - v_2(\mathbf{r})]\rho(\mathbf{r}) & (9) \end{aligned}$$

The strict inequality comes from the fact that $\Psi_1 \neq \Psi_2$. However, by exactly the same logic, we also have that

$$E_2 < E_1 + \int d\mathbf{r}\,[v_2(\mathbf{r}) - v_1(\mathbf{r})]\rho(\mathbf{r}) \tag{10}$$

Which leads to an absurdity

$$\begin{aligned} E_1 + E_2 &< E_2 + \int d\mathbf{r}\,[v_1(\mathbf{r}) - v_2(\mathbf{r})]\rho(\mathbf{r}) + E_1 + \int d\mathbf{r}\,[v_2(\mathbf{r}) - v_1(\mathbf{r})]\rho(\mathbf{r}) & (11)\\ &< E_2 + E_1 & (12) \end{aligned}$$

Therefore there cannot exist two local potentials differing by more than an additive constant which have the same ground-state density. Note that this proof, unlike the original HK proof, does not assume non-degenerate ground states.

The fact that the ground state electron density contains sufficient information to uniquely specify the Hamiltonian can be understood in simple terms:

1. The density specifies the number of electrons:

$$\int d\mathbf{r}\rho(\mathbf{r}) = n$$

2. The cusps in the density specify the number of nuclei, the nuclear charges and where they are:

$$\frac{\partial \rho(\mathbf{R}_I + \mathbf{r})}{\partial r}\bigg|_{r=0} = -2Z_I \rho(\mathbf{R}_I)$$

2.1.2 HK-2 (as redefined by Levy and Leib)

We can define an energy functional that maps a density to an energy. The energy is greater than or equal to the exact ground state energy, with the equality holding for the exact ground state density.

Consider the usual variational principle

$$E_0 = \min_{\Psi} \langle \Psi | \hat{F} + \hat{V} | \Psi \rangle \tag{13}$$

where the search is over normalised n-electron wavefunctions. This set of wavefunctions can be partitioned into subsets, where the all the wavefunctions in a subset integrate to give the same density $\Psi \rightarrow \rho$. Thus

$$\begin{aligned} E_0 &= \min_{\Psi} \langle \Psi | \hat{F} + \hat{V} | \Psi \rangle & (14) \\ &= \min_{\rho} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{F} + \hat{V} | \Psi \rangle & (15) \\ &= \min_{\rho} \left\{ \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{F} | \Psi \rangle + \int d\mathbf{r}\, v(\mathbf{r}) \rho(\mathbf{r}) \right\} & (16) \\ &= \min_{\rho} \left\{ F[\rho] + \int d\mathbf{r}\, v(\mathbf{r}) \rho(\mathbf{r}) \right\} & (17) \end{aligned}$$

The variational energy functional is

$$\begin{aligned} E[\rho] &= F[\rho] + \int d\mathbf{r}\, v(\mathbf{r}) \rho(\mathbf{r}) & (18) \\ E_0 &= \min_{\rho} E[\rho] & (19) \end{aligned}$$

Note that the search over densities must only be over those that can result from a n-electron wavefunction, i.e. n-representable densities. The functional $F[\rho]$ is the universal density functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{F} | \Psi \rangle \tag{20}$$

If we knew the form of $F[\rho]$, we would then be able to perform varitional searches for the exact ground state energy using the density alone, with no reference to the wavefunction! Density Functional Theory is primariliy concerned with finding good approximations to $F[\rho]$.

3 Kohn-Sham Theory

Although the DFT introduced above promises an enormous simplification, two problems remain. Firstly, we need to perform searches over only those densities that can result from a n-electron wavefunction. Secondly, we need to find good approximations to $F[\rho]$. In particular, the kinetic energy contribution to $F[\rho]$ is large and very hard to approximate. The Kohn–Sham approach goes a long way to solving both of these problems.

In Kohn–Sham theory, we introduce a ficticious system of n non-interacting electrons. The wavefunction for this system is simply a single Slater determinant.

$$|\Phi_s\rangle = |\phi_1 \dots \phi_n\rangle \tag{21}$$

This device serves two purposes. Firstly, any n-representable density ρ can always be obtained from a single slater determinant of n spin-orbitals. Secondly, we can extract a large component of the kinetic energy contribution to $F[\rho]$. We write

$$F[\rho] = T_s[\rho] + E_{Hxc}[\rho] \tag{22}$$

$$T_s[\rho] = \min_{\Phi_s \to \rho} \langle \Phi_s|\hat{T}|\Phi_s\rangle \tag{23}$$

where we have introduced the non-interacting kinetic energy functional $T_s[\rho]$, defined in terms of a seach over the Kohn–Sham determinants that integrate to density ρ. This allows us to write

$$\begin{aligned}
E_0 &= \min_{\rho} \left\{ F[\rho] + \int d\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r}) \right\} && (24)\\
&= \min_{\rho} \left\{ \min_{\Phi_s \to \rho} \langle \Phi_s|\hat{T}|\Phi_s\rangle + E_{Hxc}[\rho] + \int d\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r}) \right\} && (25)\\
&= \min_{\rho} \min_{\Phi_s \to \rho} \left\{ \langle \Phi_s|\hat{T} + \hat{V}|\Phi_s\rangle + E_{Hxc}[\rho_\Phi] \right\} && (26)\\
&= \min_{\Phi_s} \left\{ \langle \Phi_s|\hat{T} + \hat{V}|\Phi_s\rangle + E_{Hxc}[\rho_\Phi] \right\} && (27)
\end{aligned}$$

The search over n-representable densities has become a search over Kohn–Sham determinants and we now only require good approximations to the functional $E_{Hxc}[\rho]$.

Note the striking similarity with Hartree–Fock theory:

$$E_{\mathrm{HF}} = \min_{\Phi} \langle \Phi|\hat{T} + \hat{V} + \hat{V}_{ee}|\Phi\rangle \tag{28}$$

In Kohn–Sham theory, the electron-electron repulsion operator is replaced with a functional of the density, which is defined such that the exact ground state energy is obtained by variational minimisation.

We can further decompose the remaining unknown part of the universal functional

$$E_{Hxc}[\rho] = E_H[\rho] + E_{xc}[\rho] \tag{29}$$

$$E_H[\rho] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \tag{30}$$

where $E_H[\rho]$ is the Hartree energy functional, which is simply the classical electrostatic repulsion energy for the charge distribution $\rho(\mathbf{r})$ and can be computed exactly. This is by far the largest contribution to $E_{Hxc}[\rho]$, but it should be noted that the Hartree energy functional contains the unphysical contribution of an electron repelling itself, referred to as the self-interaction energy. Approximations to the exchange correlation functional $E_{xc}[\rho]$ are the subject of L8.

3.1 The Kohn–Sham equations

In Kohn–Sham theory we use the orbitals of a system of n non-interacting electrons to search over densities to minimise the Kohn–Sham energy functional

$$E_0 = \min_{\Phi_s} \left\{ \langle \Phi_s | \hat{T} + \hat{V} | \Phi_s \rangle + E_{Hxc}[\rho_\Phi] \right\} = \min_{\Phi_s} \left\{ \sum_i^n \langle \phi_i | \hat{h} | \phi_i \rangle + E_{Hxc}[\rho_\Phi] \right\} \tag{31}$$

where

$$\rho_\Phi(\mathbf{r}) = \sum_i^n \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \tag{32}$$

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \tag{33}$$

In L2 we minimised the Hartree–Fock energy with respect to the Hartree–Fock orbitals and obtained the Fock equation. The Kohn–Sham equations are obtained in an analogous way, however, here we must use calculus of variations since we cannot assume a particular structure of $E_{Hxc}[\rho]$. We are optimising the energy subject to the constraint of orthonormal spin-orbitals and therefore start from the Lagrangian

$$L[\Phi] = \sum_i^n \langle \phi_i | \hat{h} | \phi_i \rangle + E_{Hxc}[\rho_\Phi] - \sum_{ij}^n \epsilon_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \tag{34}$$

The stationary condition is

$$\frac{\delta L[\Phi]}{\delta \phi_i^*} = 0 \tag{35}$$

Functional Derivatives

Functionals $F[f]$ map a function $f(x)$ to a number. An infinitesimal variation δf of f leads to an infinitesimal variation of F, which can be expressed as

$$\delta F[f] = \int dx \, \frac{\delta F}{\delta f} \delta f$$

This defines the functional derivative of $F[f]$ with repect to f: $\frac{\delta F}{\delta f}$
In the calculus of variations, functionals are usually expressed in terms of an integral of functions, their arguments, and their derivatives. For example

$$L[f] = \int dx \, F[x, f, f', f'', \ldots]$$

The formula for the functional derivative is

$$\frac{\delta F}{\delta f} = \frac{\partial F}{\partial f} - \frac{\partial}{\partial x} \frac{\partial F}{\partial f'} + \frac{\partial^2}{\partial x^2} \frac{\partial F}{\partial f''} - \ldots$$

For a functional $F[f]$ where f is itself a functional of another function $g(x)$, we have the chain rule

$$\frac{\delta F}{\delta g(x)} = \int dx' \, \frac{\delta F}{\delta f(x')} \frac{\delta f(x')}{\delta g(x)}$$

Exercise 1
Consider the Functional

$$F[\{\phi_i\}] = \sum_i^n \langle\phi_i| - \tfrac{1}{2}\nabla^2 + v(\mathbf{r})|\phi_i\rangle - \sum_{ij}^n \epsilon_{ij}(\langle\phi_i|\phi_j\rangle - \delta_{ij})$$

Show that the Funtional derivative is

$$\frac{\delta F}{\delta\phi_i^*} = [-\tfrac{1}{2}\nabla^2 + v(\mathbf{r})]\phi_i(\mathbf{r}) - \sum_j^n \epsilon_{ij}\phi_j(\mathbf{r})$$

Evaluating the functional derivative we obtain

$$\frac{\delta L}{\delta\phi_i^*} = \hat{h}\phi_i(\mathbf{r}) + \frac{\delta E_{Hxc}[\rho]}{\delta\phi_i^*} - \sum_j^n \epsilon_{ij}\phi_j(\mathbf{r}) = 0 \tag{36}$$

We can evaluate the functional derivative of E_{Hxc} via the chain rule

$$\begin{aligned}\frac{\delta E_{Hxc}[\rho]}{\delta\phi_i^*(\mathbf{r})} &= \int d\mathbf{r}'\, \frac{\delta E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r}')}{\delta\phi_i^*(\mathbf{r})} \qquad (37)\\ &= \int d\mathbf{r}' v_{Hxc}(\mathbf{r}')\phi_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') = v_{Hxc}(\mathbf{r})\phi_i(\mathbf{r}) \qquad (38)\end{aligned}$$

where we have introduced the Hartree-exchange-correlation potential $v_{Hxc}(\mathbf{r})$

$$v_{Hxc}(\mathbf{r}) = \frac{\delta E_{Hxc}[\rho]}{\delta\rho(\mathbf{r})} \tag{39}$$

Just as for Hartree–Fock theory, since all the terms are Hermitian and the density is invariant with respect to rotations among the occupied orbitals, we are free to select orbitals that diagonalise the matrix of Lagrange multipliers. We arrive at the Kohn–Sham equations

$$\left(\hat{h} + v_{Hxc}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \tag{40}$$

Since $v_{Hxc}(\mathbf{r})$ is a functional of the density, these equations must be solved self-consistently. Physically, $\hat{h} + v_{Hxc}(\mathbf{r})$ defines a system of n non-interacting electrons in a modified effective external potential that ensures that its ground-state density $\rho(\mathbf{r})$ is the same as the exact ground-state density of the physical system of n interacting electrons. After solution, the orbitals ϕ_i are the Kohn–Sham orbitals and ε_i are the Kohn–Sham orbital energies.

Exercise 2
Show that the funtional derivative of the Hartree energy functional is

$$\frac{\delta E_H}{\delta\phi_i^*} = v_H(\mathbf{r})\phi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int d\mathbf{r}'\, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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4 Implementation of KS-DFT

The Kohn–Sham equations are operationally very similar to the Hartree–Fock equations and the computer implementation of KS theory follows that of Hartree–Fock theory very closely, with many common elements. In particular, the orbitals are expanded as a linear combination of Gaussian atom-centred fuctions. Recall that in the AO basis the Fock matrix is

$$F_{\mu\nu} = H_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu} \tag{41}$$

$$H_{\mu\nu} = \langle \eta_\mu | \hat{h} | \eta_\nu \rangle \tag{42}$$

$$J_{\mu\nu} = \sum_j^n \langle \eta_\mu j | r_{12}^{-1} | \eta_\nu j \rangle \tag{43}$$

$$K_{\mu\nu} = \sum_j^n \langle \eta_\mu j | r_{12}^{-1} | j \eta_\nu \rangle \tag{44}$$

The Kohn-Sham matrix is

$$F_{\mu\nu} = H_{\mu\nu} + J_{\mu\nu} + V_{\mu\nu}^{xc} \tag{45}$$

$$V_{\mu\nu}^{xc} = \langle \eta_\mu | v_{ex}(\mathbf{r}) | \eta_\nu \rangle \tag{46}$$

Typically, $v_{ex}(\mathbf{r})$ does not have a functional form ammenable to analytic integration and the matrix elements $V_{\mu\nu}^{xc}$ are computed by numerical integration on a grid (quadrature).

$$V_{\mu\nu}^{xc} \approx \sum_k w_k \, \eta_\mu^*(\mathbf{r}_k) v_{ex}(\mathbf{r}_k) \eta_\nu(\mathbf{r}_k) \tag{47}$$

where $\mathbf{r}_k$ and w_k are quadrature points and weights. For polyatomic molecules,the multicenter numerical integration scheme of Becke (1988) is generally used.

5 Time-Dependent KS-DFT

Consider the time-dependent electronic Schrödinger equation with an external time-dependent potential

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\hat{F} + \hat{V}(t)\right)|\Psi(t)\rangle \tag{48}$$

Runge and Gross (1984) showed that, for a given initial wave function $|\Psi(0)\rangle$, the time-dependent density $\rho(\mathbf{r}, t)$ determines the time-dependent potential $v(\mathbf{r}, t)$ up to an arbitrary additive time function. This enables us to set up a time-dependent non-interacting KS system

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) = \left(-\tfrac{1}{2}\nabla^2 + v(\mathbf{r}, t) + v_{Hex}(\mathbf{r}, t)\right)\phi_i(\mathbf{r}, t) \tag{49}$$

where the time-dependent KS potential is such that density of the KS system matches that of the exact density at every point in time.

We are interested in what happens to a molecule when placed in a weak oscillating electric field. Consider a time-periodic potential of single frequency $v_{ext}(\mathbf{r}', \omega)$. In the Fourier domain, the response of the density is

$$\delta\rho(\mathbf{r}, \omega) = \chi(\mathbf{r}, \mathbf{r}', \omega)\delta v_{ext}(\mathbf{r}', \omega) \tag{50}$$

where the $\chi(\mathbf{r},\mathbf{r}',\omega)$ is the frequency dependent linear response function which describes the change in the density at $\mathbf{r}$ when the external potential undergoes a small change at $\mathbf{r}'$. We have

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta\rho(\mathbf{r},\omega)}{\delta v_{ext}(\mathbf{r}',\omega)} \qquad \text{and} \qquad \chi^{-1}(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta v_{ext}(\mathbf{r}',\omega)}{\delta\rho(\mathbf{r},\omega)} \tag{51}$$

For the KS system, changes in the density are connected to changes in both the external potential and the Kohn–Sham potential. The KS non-interacting linear-response function is

$$\chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega) = \frac{\delta v_{ext}(\mathbf{r}',\omega)}{\delta\rho(\mathbf{r},\omega)} + \frac{\delta v_{Hex}(\mathbf{r}',\omega)}{\delta\rho(\mathbf{r},\omega)} \tag{52}$$

$$= \chi^{-1}(\mathbf{r},\mathbf{r}',\omega) + f_{Hex}(\mathbf{r},\mathbf{r}',\omega) \tag{53}$$

where we have introduced the Hartree-exchange-correlation kernel $f_{Hex}(\mathbf{r},\mathbf{r}',\omega)$. Both $\chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega)$ and $f_{Hex}(\mathbf{r},\mathbf{r}',\omega)$ can be computed. Thus the interacting linear-response function $\chi(\mathbf{r},\mathbf{r}',\omega)$ is found from the Dyson-like response equation

$$\chi^{-1}(\mathbf{r},\mathbf{r}',\omega) = \chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega) - f_{Hex}(\mathbf{r},\mathbf{r}',\omega) \tag{54}$$

$\chi(\mathbf{r},\mathbf{r}',\omega)$ has poles at the excitation energies $E_n - E_0 = \omega_n$. If the frequency dependence of the Hartree-exchange-correlation kernel is neglected (called the adiabatic approximation), then only the single-electron excitations are taken into account (double excitations and higher are missing).