OVERVIEW OF DENSITY FUNCTIONAL THEORY FOR SUPERCONDUCTORS

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Intisari

SEKILAS TENTANG TEORI FUNGSIONAL KERAPATAN ELEKTRON PADA SUPERKONDUKTOR. Teori fungsional kerapatan elektron atau *density functional theory* (DFT) digunakan untuk menjelaskan interaksi elektron pada material superkonduktor. Makalah ini membahas aspek mendasar untuk inisiasi penggunaan DFT, seperti aproksimasi kerapatan lokal atau *local density approximation* (LDA) serta transformasinya menjadi sistem yang bergantung terhadap waktu atau *time dependent system* (TDDFT) dan kondisi superkonduktif atau *superconducting state* (SCDFT). Teorema Hamiltonian dan Kohn-Sahm dipergunakan untuk menghitung energi sistem yang berinteraksi maupun yang tidak berinteraksi. Persamaan Schrödinger yang independen terhadap waktu diselesaikan untuk mengetahui posisi elektron terisi maupun tidak terisi serta respon mereka terhadap pengaruh eksternal seperti medan optik. Pemodelan menghasilkan konstruksi dari LDA superkonduktor.

Kata kunci : Teori fungsional kerapatan elektron, Aproksimasi kerapatan lokal, Sistem Hamiltonian, Teorema Kohn-Sahm, Superkonduktor

Abstract

OVERVIEW OF DENSITY FUNCTIONAL THEORY FOR SUPERCONDUCTORS. *The density functional theory (DFT) has been utilized to describe the electron interaction in superconducting materials. This paper discusses the fundamental aspects to begin with the DFT, including local density approximation (LDA) as well as its necessary transformation into time dependent system (TDDFT) and superconducting state (SCDFT). The Hamiltonian and Kohn-Sahm theorems along with Helmann-Feymann theorem are utilized to yield the energy of interacting and non-interacting systems. The procedures begins with the utilization of time-independent Schrödinger equation which is solved for occupied and unoccupied states. The equation is also computed against linear and non-linear responses of the material system to the external forces such as optical field. The results indicate construction of an LDA for superconductors.*

Keywords : Density functional theory, Local density approximation, Hamiltonian system, Kohn-Sahm theorem, Superconductor

INTRODUCTION

A successful approach that is common in electronic structure calculations is to use ab initio pseudopotentials within density functional theory (DFT). DFT has been very popular for the numerical calculation in the area of solid-state physics since 1970s. This DFT approach has been used to predict mechanical, chemical, and electronic properties of many classes of solids, liquids, molecules, and more. In density functional theory, the original N-electron problem is converted into an effective one-electron problem, where all non-classical electron interactions (namely, exchange and correlation) are replaced by an additive one-electron potential that is a functional of the charge density. While this mapping is formally exact, it is approximate in practice because the exact functional is unknown. DFT possesses limitation in properly describing intermolecular interactions characterized by van der Waals forces (dispersion of noble gases' atoms[1]), biomolecular interaction[2], as well as calculations in band gap of semiconductors. Alterations of the functional and inclusion of additive terms have become a recent progress in the attempts to further develop and improve DFT[3-6]. A common approximation to this functional, which is used in this paper, is the Local Density Approximation (LDA) where the exchange-correlation functional is defined as a local function of the charge density. However, because traditional time-independent DFT is inherently a ground-state theory it is not suitable for the computation of electronic excitations in general, and optical properties in particular. A generalized, *time-dependent* DFT (TDDFT) formalism has been developed which allows the computation of excited state properties. This approach was applied successfully to a wide range of atoms and small molecules. Optical properties of larger systems of molecules, clusters, or "quantum dots" (small fragments of bulk material) in the range of many hundreds of atoms are much harder to address despite their outstanding importance in physics. This is primarily due to severe computational limitations.

In 1988, triggered by the remarkable discovery of the high-*Tc* materials, Oliveira, Gross and Kohn (OGK) proposed a density functional theory for the superconducting state (SCDFT). Up to now, the success of SCDFT has been fairly limited, essentially due to the nonexistence of adequate xc functionals. Several recent developments may, however, bring SCDFT to a much wider audience.

APPROXIMATE DENSITY FUNCTIONAL

A well known method for the derivation of approximate density functionals is the coupling constant integration technique, which provides a relation between the interacting and the non-interacting system by introducing a Hamiltonian $\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda\hat{W}$, with V_λ defined such that for each $\lambda \in [0,1]$ the same ground state density ρ is obtained. In this way the fully interacting system corresponds to $\lambda=1$ with external potential $v = V_{\lambda=1}$, while the Kohn-Sham system is described by $\lambda=0$ with $v_S = V_{\lambda=0}$. Denoting the ground-state for coupling constant λ by Ψ_λ, application of the Helmann-Feynman theorem yields a relation between the energy of the interacting and non-interacting system,

$$\frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda} = <\Psi_\lambda | \frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda} | \Psi_\lambda> = <\Psi_\lambda | \hat{W} | \Psi_\lambda> + \frac{\mathrm{d}}{\mathrm{d}\lambda} \int v_\lambda(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}, \qquad (2.1)$$

$$E(1) = E(0) + \int_0^1 <\Psi_\lambda | \hat{W} | \Psi_\lambda> \mathrm{d}\lambda + \int \rho(\mathbf{r})\big(v(\mathbf{r}) - v_S(\mathbf{r})\big)\mathrm{d}\mathbf{r}, \qquad (2.2)$$

where $E(0)$ corresponds to the artificial non-interacting energy, and $E(1)$ to the ground state energy of the interacting system. Using (2.3) – (2.5)

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})\mathrm{d}\mathbf{r} + F_{HK}[\rho],$$
$$F_{HK}[\rho] = <\Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho]> \qquad (2.3)$$

$$E_{v_S}[\rho] = T_S[\rho] + \int \rho(\mathbf{r})v_S(\mathbf{r})\mathrm{d}\mathbf{r},$$
$$T_S[\rho] = <\Psi_S | \hat{T} | \Psi_S> \qquad (2.4)$$

$$F_{HK}[\rho] = T_s[\rho] + \frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 +$$
$$E_{xc}[\rho] = T_s[\rho] + W_H[\rho] + E_{xc}[\rho] \qquad (2.5)$$

the following expression for the xc-energy can be obtained

$$E_{xc}[\rho] = \int_0^1 <\Psi_\lambda | \hat{W} | \Psi_\lambda> \mathrm{d}\lambda$$

$$-\frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

$$=\frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$\left(\int_0^1 g_\lambda(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\lambda-1\right)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \qquad (2.6)$$

Good approximations to E_{XC} can thus be obtained by constructing good approximations to the lambda integrated coupling constant pair correlation function $g\lambda$[7-10].

FORMALISM

The procedure begins with the solution of the time-independent Schrödinger equation, using the pseudo-potential DFT formulation in the domain Ω,

$$\left(-\frac{\Delta}{2}+\sum_{R_\alpha}V_{ps}(r-R_\alpha)+V_H(\rho(r))+V_{xc}(\rho(r))\right)$$

$$\psi_n(r)=\varepsilon_n\psi_n(r) \qquad (3.1)$$

In the above equation, ψ_n and ε_n denote the nth single-electron eigenfunction and eigenvalue respectively. The charge density, denoted by $\rho(r)$, is the sum of squares of the eigenfunctions $\psi_n(r)$ associated with the occupied states. Finally, V$_H$ is the Hartree (electron-electron) interaction potential, V$_{ps}$ is the pseudo-potential which represents the interactions between ions located in R_α and V$_{xc}$ is the exchange-correlation potential. The above equation is solved for all occupied states and a number on unoccupied states resulting in a set of eigenpairs ε_j,ψ_j. The eigenfunctions are then used to assemble the coupling matrix *K* in the form:

$$K_{ij,kl}=2\int_\Omega\int_\Omega \bar{\psi} i(r)\psi j(r)\left(\frac{1}{|r-r'|}+\frac{dV_{xc}(\rho(r))}{d\rho(r)}\delta(r-r')\right)$$

$$\psi k(r')\bar{\psi} l(r')drdr' \qquad (3.2)$$

where Ω is the physical domain, which is a subset of $\Re^3$. Given this, the optical absorption spectrum of a system of molecules is computed as, $QF_1=\omega_1^2F1$ where

$$Qij,kl=\delta_{ik}\delta_{jl\omega_{kl}^2}+2\sqrt{\lambda_{ij\omega ij}}K_{ij,kl}\sqrt{\lambda_{kl\omega kl}} \qquad (3.3)$$

with $\lambda_{ij}=f(\varepsilon_i)-f(\varepsilon_j)$ is the difference between occupied states (*f* denotes the Fermi-Dirac function) and $\omega_{ij}=\varepsilon_i-\varepsilon_j$. The term ω_{ij} is directly related to the optical transition energy.

The eigenvalues and eigenfunctions of the matrix Q(ω) are then computed and, finally, the oscillator strengths associated with the transition energy ω_I are obtained as follows: $f_I=\frac{2}{3}\sum_{\beta=\{x,y,z\}}\left|B_\beta^TR^{1/2}F_I\right|$. Here, $R_{ij,kl}(\omega)=\delta_{ik}\delta_{jl}\lambda_{kl\omega kl}$ and $(B_\beta)_{ij}=\int\psi_i^*(r)\beta\psi_j(\mathbf{r})d\mathbf{r}$ for the three cartesian directions $\beta=\{x,y,z\}$[7-10].

LINEAR RESPONSE

The most common application is the response to a weak long-wave length optical field,

$$\delta\upsilon_{ext}(\mathbf{r}t)=-\xi\exp(i\omega t)z \qquad (4.1)$$

In the general case of the response of the ground-state to an arbitrary weak external field, the system's first-order response is characterized by the non-local susceptibility

$$\delta\eta_\delta(\mathbf{r}t)=\sum_{\sigma'}\int dt'\int d^3r'\chi_{\sigma\sigma'}[\eta_0]$$

$$(\mathbf{r},\mathbf{r}';t-t')\delta\upsilon_{ext\sigma'}(\mathbf{r}'t') \qquad (4.2)$$

This susceptibility χ is a functional of the *ground-state* density, $\eta_0(\mathbf{r})$. A similar equation describes the densityresponse in the KS system:

$$\delta\eta_{\delta}(\mathbf{r}t) = \sum_{\sigma'}\int dt'\int d^3r'\chi_{s\sigma\sigma'}[\eta_0]$$
$$(\mathbf{r},\mathbf{r}';t-t')\delta\upsilon_{s\sigma'}(\mathbf{r}'t') \qquad (4.3)$$

Here χ_s is the Kohn-Sham response function, constructed from KS energies and orbitals:

$$\chi_{s\sigma\sigma'}(\mathbf{r}\mathbf{r}'\omega) = \delta_{\sigma\sigma'}\sum_q\left\{\frac{\Phi_{q\sigma}(\mathbf{r})\Phi^*_{q\sigma'}(\mathbf{r}')}{\omega-\omega_q+i0_+} - \right.$$

$$\left.\frac{\Phi^*_{q\sigma}(\mathbf{r})\Phi_{q\sigma'}(\mathbf{r}')}{\omega+\omega_q-i0_+}\right\} \qquad (4.4)$$

where q is a double index, representing a transition from occupied KS orbital *i* to unoccupied KS orbital $\alpha, \omega_{q\sigma} = \varepsilon_{\alpha\sigma} - \varepsilon_{i\sigma}$ and $\Phi_{q\sigma}(\mathbf{r}) = \phi^*_{i\sigma}(\mathbf{r})\phi_{\alpha\sigma}(\mathbf{r})$. 0_+ means the limit as 0_+ goes to zero from above (i.e., along the positive real axis). Thus χ_s is completely determined by the ground-state KS potential. It is the susceptibility of the non-interacting electrons sitting in the KS ground-state potential.

Since $\delta\upsilon_{HXC\sigma}(\mathbf{r})$ is due to an infinitesimal change in the density, it may be written in terms of its functional derivative, i.e.,

$$\delta\upsilon_{HXC\delta}(\mathbf{r}t) = \sum_{\sigma'}\int d^3t'\int dtf_{HXC\sigma\sigma'}$$
$$(\mathbf{r}\mathbf{r}',t-t')\delta\eta_{\sigma'}(\mathbf{r}'t') \qquad (4.5)$$

After Fourier transforming in time, the central equation of TDDFT linear response is a Dyson-like equation for the true χ of the system[7-10]:

$$\chi_{\sigma\sigma'}(\mathbf{r}\mathbf{r}'\omega) = \chi_{S\sigma\sigma'}(\mathbf{r}\mathbf{r}'\omega) + \sum_{\sigma_1\sigma_2}\int d^3r_1$$
$$\int d^3r_2\chi_{S\sigma\sigma_1}(\mathbf{r}\mathbf{r}_1\omega)$$
$$x\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + f_{XC\sigma_1\sigma_2}(\mathbf{r}_1\mathbf{r}_2\omega)\right)$$
$$\chi_{\sigma_2\sigma'}(\mathbf{r}_2\mathbf{r}'\omega) \qquad (4.6)$$

Figure 1 shows the dipole response of this simple system, which is essentially a plasmon resonance, using the linear-response equations enumerated above, and compared with a simple Runge–Kutta calculation of the response. The agreement is excellent.

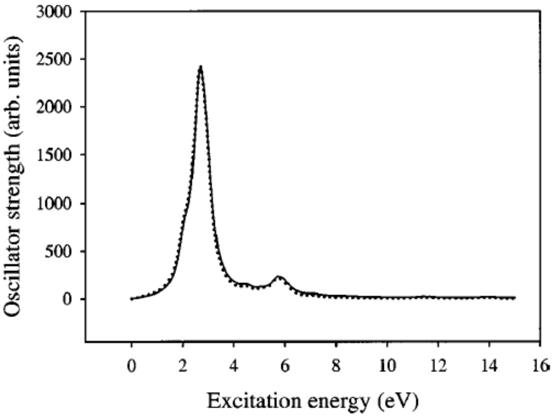

Figure 1. The dipole spectrum for a metallic (jellium) shell of density $n = 0.0088a_0^3$. The solid line shows the result of the Fourier transformed spectrum directly from the full TD Kohn–Sham equations, and the dotted line shows the results of the linearized Chebyshev propagation[11]

NONLINEAR RESPONSE

The nonlinear response functions appear in

$$p_i^{(2)}(t) = \int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2$$
$$\chi_{ijk}^{(2)}(t;t_1,t_2)E_j(t_1)E_k(t_2) \qquad (5.1)$$

and

$$p_i^{(3)}(t) = \int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\int_{-\infty}^{\infty}dt_3$$
$$\chi_{ijkl}^{(3)}(t;t_1,t_2,t_3)E_j(t_1)E_k(t_2)E_l(t_3) \qquad (5.2)$$

as not uniquely determined, since there are permutation symmetries of the applied field **E**(t) that may appear in different order. To see this for the second-order response function, we write $\chi_{ijk}^{(2)}(t;t_1,t_2)$ as the sum of a symmetric part and an antisymmetric part,

$$\chi_{ijk}^{(2)}(t;t_1,t_2) = \chi_{ijk}^{S(2)}(t;t_1,t_2) + \chi_{ijk}^{A(2)}(t;t_1,t_2) \tag{5.3}$$

where

$$\chi_{ijk}^{S(2)}(t;t_1,t_2) = \frac{1}{2}\left[\chi_{ijk}^{(2)}(t;t_1,t_2) + \chi_{ijk}^{(2)}(t;t_1,t_2)\right] \tag{5.4}$$

and

$$\chi_{ijk}^{A(2)}(t;t_1,t_2) = \frac{1}{2}\left[\chi_{ijk}^{(2)}(t;t_1,t_2) + \chi_{ijk}^{(2)}(t;t_1,t_2)\right] \tag{5.5}$$

which are symmetric and antisymmetric under the interchanging the pairs of variables (*j*, t$_1$) and (*k*, t$_2$) [7-10].

TDDFT ON EXCITATIONS

The KS excitations are the energy different between the excited states and the ground state. Since the KS system only has the same ground state density as the real system, it can not give correct excitation information from its excited orbitals. Even for the ground state, the total energy of the orbitals are not the true ground state energy.

For the KS system of the toy model, the orbitals are the solutions to $\left\{-\frac{1}{2}\frac{d^2}{dx^2} + \upsilon_s(x)\right\}\phi(x) = \in\phi(x)$. Suppose the ground state orbital is $\phi_0(x)$, with energy $\in_0$, and the excitation are $\phi_1(x), \phi_2(x), \phi_3(x)$, and so on, with energies of $\in_1, \in_2$ and $\in_3$. So the singlet states are :

$$\Phi_{(0,0)}(x_1,x_2) = \phi_0(x_1)\phi_0(x_2), \tag{6.1}$$

ground state,

$$\Phi_{(0,1)}(x_1,x_2) = \frac{1}{\sqrt{2}}[\phi_0(x_1)\phi_1(x_2) + \phi_1(x_1)\phi_0(x_2)], \tag{6.2}$$

first excited state,

$$\Phi_{(1,1)}(x_1,x_2) = \phi_1(x_1)\phi_1(x_2), \tag{6.3}$$

second excited state,

$$\Phi_{(0,2)}(x_1,x_2) = \frac{1}{\sqrt{2}}[\phi_0(x_1)\phi_2(x_2) + \phi_2(x_1)\phi_0(x_2)] \tag{6.4}$$

third excited state,

....

The energies of the KS system are the summation of the orbital energies, so

$$E_{(0,0)} = 2\in_0 \tag{6.5}$$

$$E_{(0,1)} = \in_0 + \in_1 \tag{6.6}$$

$$E_{(1,1)} = 2\in_0 \tag{6.7}$$

$$E_{(0,2)} = \in_0 + \in_2 \tag{6.8}$$

Thus the KS transition frequencies are

$$\omega_{(0,1)} = \in_1 - \in_0 \tag{6.9}$$

$$\omega_{(1,1)} = 2(\in_1 - \in_0) \tag{6.10}$$

$$\omega_{(0,2)} = \in_2 - \in_0 \tag{6.11}$$

And we can see that (0, 1) and (0, 2) are single excitations and (1, 1) is a double excitation since both of the two electrons are excited from ground state to the first excited state[7-10].

LOCAL SPIN DENSITY APPROXIMATION

To properly describe superconductivity we clearly have to take into account the electronphonon interaction. In the original OGK formulation this interaction was modeled by a phonon-mediated effective electron-electron attraction of the form

$$\hat{W} = -\sum_{\sigma\sigma'} \int d^3r_1 \int d^3r_2 \int d^3r_3 \int d^3r_4$$
$$\hat{\psi}_\sigma^+(r_1)\hat{\psi}_{\sigma'}^+(r_2)\omega(r_1, r_2, r_3, r_4)$$
$$\hat{\psi}_{\sigma'}(r_3)\hat{\psi}_\sigma(r_4) \qquad (7.1)$$

To the Hamiltonian OGK added the term

$$\hat{\Delta} = -\Big[\int d^3r \int d^3r' \Delta_0^*(r, r')$$
$$\hat{\psi}_\uparrow(r)\hat{\Psi}_\downarrow(r') + H.c.\Big] \qquad (7.2)$$

This term is only required to break the gauge symmetry of the system, and can be taken to zero at the end of the derivation. Alternatively, it can be viewed as describing a pairing field induced by a nearby superconductor.

The construction of SCDFT follows a parallel route to the derivation of spin-DFT. In this latter theory one uses as basic variables the spin-densities, η_σ, or equivalently, the total density $\eta = \eta_\uparrow + \eta_\downarrow$ and the magnetization density $m = -\mu_0(\eta_\uparrow - \eta_\downarrow$. The second density, *m*, can be viewed as a magnetic order parameter which is zero above a certain critical point and non-zero below, marking the transition from the non-magnetic to the magnetic phase. In a similar way, we will use as basic variables in SCDFT the “normal” density

$$\eta(r) = \sum_\sigma \left\langle \hat{\psi}_\sigma^+(r)\hat{\psi}_\sigma(r) \right\rangle \qquad (7.3)$$

and a non-local, “anomalous” density

$$\chi(r, r') = \left\langle \hat{\psi}_\uparrow(r)\hat{\psi}_\downarrow(r') \right\rangle \qquad (7.4)$$

As in ordinary DFT, we now introduce a system of non-interacting electrons (the Kohn-Sham system) described by the Hamiltonian

$$\hat{\mathrm{H}}_{KS} = \sum_\sigma \int d^3r \hat{\psi}_\sigma^+(r) \left[-\frac{\nabla^2}{2} + \upsilon_{KS}(r) - \mu \right] \hat{\psi}_\sigma(r)$$
$$-\left[\int d^3r \int d^3r' \Delta_{KS}^*(r, r')\hat{\psi}_\uparrow(r)\hat{\psi}_\downarrow(r') + H.c. \right] (7.5)$$

The Kohn-Sham potentials $\{\upsilon_{KS}\Delta_{KS}\}$ are chosen such that the pair of densities of the Kohn-Sham system equals the densities of the interacting system, $\{\eta, \chi\}$. They are given by

$$\upsilon_{KS}[\eta, \chi](r) = \upsilon(r) + \int d^3r' \frac{\eta(r')}{|r - r'|} +$$
$$\upsilon_{xc}[\eta, \chi](r) \qquad (7.6)$$

$$\Delta_{KS}[\eta, \chi](r, r') = \Delta(r, r') - \frac{\chi(r, r')}{|r - r'|} +$$
$$\Delta_{xc}[\eta, \chi](r, r') \qquad (7.7)$$

The xc potentials are formally defined as functional derivatives of the xc free-energy Functional $F_{xc}[\eta, \chi]$

$$\upsilon_{xc}[\eta, \chi](r) = \frac{\delta F_{xc}[\eta, \chi]}{\delta n(r)} \qquad (7.8)$$

$$\Delta_{xc}[\eta, \chi](r, r') = -\frac{\delta F_{xc}[\eta, \chi]}{\delta \chi^*(r, r')} \qquad (7.9)$$

Finally, $F_{xc}[\eta, \chi]$ is defined through the expression

$$F[\eta, \chi] = \mathrm{T}_S[\eta, \chi] - \frac{1}{\beta} S_S[\eta, \chi] + \frac{1}{2} \int d^3r$$
$$\int d^3r' \frac{\eta(r)\eta(r')}{|r - r'|} + \int d^3r \int d^3r' \frac{|\chi(r, r')|^2}{|r - r'|} +$$
$$F_{xc}[\eta, \chi] \qquad (7.10)$$

The LDA functional for superconductors (SCLDA) can be constructed in analogy to the local spin density approximation (LSDA), with the anomalous density playing the role of the spin-magnetization density in the LSDA. The key ingredient of the SCLDA is the xc energy per particle of the uniform gas that turns out to be a function of the normal density n, and a functional of the anomalous density $\chi(r - r^{'})$, i.e.

$$\varepsilon_{xc}^{unif} = \varepsilon_{xc}^{unif}\left[\eta, \chi(r - r^{'})\right] \qquad (7.11)$$

In this section we will make a brief detour and examine the construction of the LSDA. This construction will then serve as a template for the development of the LDA for superconductors. The spin local density approximation (LSDA) to Fxc is then defined by

$$F_{xc}^{LSDA}[\eta(r), m(r)] = \int d^3 r\,\eta(r)\,\varepsilon_{xc}^{unif}(\eta, m)\Big|_{\substack{\eta=\eta(r)\\ m=m(r)}} \qquad (7.12)$$

where $\varepsilon_{xc}^{unif}(\eta, m)$ is the xc energy per particle of an electron-gas of density η and magnetization m.

We now construct the LDA for superconductors (SCLDA) in close analogy to the LSDA. The homogeneous electron gas is exposed to an external pairing field Δ. To preserve the translational invariance of the uniform gas, Δ is chosen to depend on the difference $(r - r^{'})$. As a consequence, the induced order parameter $\chi(r - r^{'})$ is translationally invariant as well. It is therefore convenient to work in Fourier space. The Fourier transform of the anomalous density is

$$\chi(k) = \int d^3 s e^{iks} \chi(s) \qquad (7.13)$$

where $s = r - r^{'}$ is the relative coordinate of the Cooper pair. (The Fourier transform of the pair potential is defined in a similar way.) The SCLDA is then defined as

$$F_{xc}^{SCLDA}[\eta(\Re), \chi(\Re, k)] = \int d^3\Re\,\eta(\Re)\,\varepsilon_{xc}^{unif}[\eta, \chi(k)]\Big|_{\substack{\eta=\eta(\Re)\\ \chi=\chi w(\Re,k)}} \qquad (7.14)$$

where $\Re$ represents the center of mass of the Cooper pair, $\Re = (r + r^{'})/2$. The function $\chi w(\Re, k)$ is the Wigner transform of the anomalous density of the inhomogeneous system, given by

$$\chi w(\Re, k) = \int d^3 s e^{iks} \chi(\Re + \frac{s}{2}, \Re - \frac{s}{2}) \qquad (7.15)$$

This expression trivially reduces to the common LDA for non-superconducting systems in the limit $\chi \to 0$. At first sight, other definitions of an LDA for superconductors with the correct non-superconducting limit might be conceivable. However, it can be shown that (7.15) is the only correct definition. This follows from a semi-classical expansion of the total energy. The lowest-order terms in $\hbar$ are identical with the SCLDA, leading to equation (7.15)[7-12].

CONCLUSION

In this article we reviewed two extensions of ground-state DFT, the first to time dependent systems (TDDFT), and the second to the phenomenon of superconductivity (SCDFT). The construction of both theories is similar, and follows closely the development of ordinary DFT. The first step is the election of the densities that will be used as basic variables of the theory. In TDDFT one uses the time-dependent density, $\eta(r,t)$, while in SCDFT the choice falls on the pair of densities $\{\eta(r), \chi(r, r^{'})\}$. The formal foundations are then given by a Hohenberg-Kohn like theorem and by a Kohn-Sham scheme, where the complexities of the many-body system are cast into the form of xc potentials.

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