An XAS And SCDFT Analysis of HTSC Structural Characterization for RTSC Parametrization

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Abstract

The proposal presents the performance of X-ray absorption spectroscopy (XAS) in combined local-field time-dependent density functional theory (LFTDDFT)+Bethe-Salpeter Equation (BSE) formalism within real-space Green's Function (RSGF) approach with computer programme FEFF9 beyond an independent-electron model and the superconducting DFT (SCDFT) analysis with computer programme Quantum ESPRESSO for the high critical-temperature (T_c) SC (HTSC) characterization leading to microscopic mechanism of SC in strong electron-phonon interaction coupling with sensitivity of T_c as a function of dopant content and levels to approach room-temperature SC (RTSC) exploration as unique probe of RTSC parameterization.

Keywords: XAS, LFTDDFT+BSE-RSGF approach, FEFF9, SCDFT, Quantum ESPRESSO, HTSC, RTSC

I. INTRODUCTION

The essential effect of e-e and magnetic-correlations and sensitivity of critical-temperature (T_c) of high-T_c superconductors (HTSC) as a function of dopant contents and levels, and active role of doped ions degrees of freedom in inter/intra-site/orbital planar couplings can be evolved by atomic-site specific, coordination shell selective and local structure sensitive X-ray absorption spectroscopic (XAS) [1] experimental and theoretical [2] analysis with fast ab-initio computer programme FEFF9 [3] of HTSC [4]. An extension of density functional theory (DFT) to deal with superconducting state (SC), the so called SCDFT [5-8] laying the basis of characterization of HTSC with dependence of T_c on dopant contents and levels and pseudopotential in strong e-phonon exchange interaction coupling in tubular shaped sigma/pi bands at Fermi-level (E_F) with Quantum ESPRESSO [9] computer programme clarifying the microscopic mechanism of HTSC leading to room-temperature SC (RTSC) exploration with sensitivity of T_c as a function of dopant contents and active role of doped ions degrees of freedom in inter/intra-site/orbital planar couplings. The proposal presents the performance of XAS in combined local-field time-dependent DFT (LFTDDFT)+Bethe Salpeter equation (BSE) [2] in real-space Green's function (RSGF) model using FEFF9 [3] and SCDFT analysis using Quantum ESPRESSO [9-11] computational calculations which characterizes the unique possibility of T_c of HTSC to reach RTSC as a function of dopant levels. Section II deals with XAS of SC, Section III describes SCDFT [5-9], Section IV evolves XAS and SCDFT [10-11] ab-initio computational characterization of HTSC and finally Section V concludes [9-11] the HTSC phase-transition of HTSC to RTSC with sensitivity of T_c as a function of dopant contents and levels.

II. X-RAY ABSORPTION SPECTROSCOPY (XAS) OF SUPERCONDUCTORS (SC)

The material's XAS [1,2] involves the incoming X-ray photon complete absorption rendering the photoabsorbing atom's ejected photoelectron transition from normally occupied, photoexcited, inner core-level electronic-state (K,L, M etc) – under the fully relaxed, spatially static, spherically symmetric, non-overlapping muffin-tin (MT) potential V_{eff} (r) in local density approximation (LDA) of density functional theory (DFT) of remaining (N-1) passive electrons and relaxed and screened excited core-hole potential in electric dipole-moment $\tilde{d}$ approximation semi-classical selection rules using Fermi's Golden rule of photoelectron transition– to outer, higher, unoccupied electronic-state with proper symmetry as bounded/un-bounded, atomic/molecular, discrete/extended states in multi-electron configuration interaction states of an N-electron atomic system. In the multiple photoionization of material, the system's independent-electron approximation involves the (N-1) passive electrons rapid rearrangement from initial to final frozen-state configuration. The condensed system's atomic photoabsorption coefficient $\mu(\omega)$ as a function of incident X-ray photon energy displays [1,2] the complex modulatory oscillations beyond the specific photoabsorption-threshold [called as X-ray absorption edge (XAE)] termed as X-ray absorption fine-structure (XAFS) involving the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structures (EXAFS) spectral features of an XAS spectrum. The system's XAFS analysis be within an independent-electron, short-range order (SRO), single (SS)/multiple (MS), plane (PWA)/ spherical (SWA) wave-approximation scattering in the photoelectron scattering (**ES**) [Stern in [1]] and electronic energy band-structure (**EBS**) [1] model formulism by employing Fermi's Golden rule of photoelectron transition probability rate with dynamical photoelectron Green's function propagator as energy-resolvant operator in MS path (MSP) formalism [1] in system's atomic cluster which separates interatomic contributions from central photoexcited atomic core level photoelectron Green's function and photoelectron MS Green's function from atomic environment of the atomic cluster around the central embedded atom in Local Field Time Dependent Density Functional Theory (LFTDDFT). The photoabsorption coefficient $\mu(\omega)$ beyond the independent electron ES and EBS approaches of XAS with many body effects be given by the refined formalism [2] involving XAS response function $X(r, r' \omega)$ of LFTDDFT+Bethe-Salpeter Equation (BSE) [2]

in RSGF model where expression for atomic photoabsorption-coefficient in equivalent to that of screened interaction $\tilde{d}(\mathbf{r})$ operator and many-body effects as excited core-hole-photoelectron interaction, excited core-hole life-time and its relaxation, MS Debye Waller factor (DWF) as σ_j^2 contribution as mean square relative displacements (MSRD) of atoms, dynamical photoelectron self-energy Σ(E) in Plasmon Pole (PPSE) and local X-ray field effects due to screening of X-ray field be lumped into the many pole GW Approximation self-energy (MPSE) in XAS final state rule (FSR) which incorporates the MS-matrix Kernel K in reference to Lippmann–Schwinger integral equation where G is the dynamical photoelectron propagator function and W is the Coulombic field potential.

The HTSC's atomic photoabsorption coefficient in combined LFTDDFT+BSE-RSGF [1,2] approach to XAFS of XAS be

$$\mu(\omega) = \frac{-4\pi\omega}{c} Img \int d\vec{r} d\vec{r}' \hat{d} \chi(\vec{r}, \vec{r}', \omega) \hat{d}(r) \quad \text{... (II.1)}$$

$$= \int l\psi_f > \widehat{P^\dagger}.\vec{r}.ImgG(\vec{r}, \vec{r}', E+\omega).\hat{P}.\vec{r}.\overrightarrow{dr}\overrightarrow{dr'} \quad \text{... (II.2)}$$

$$= -(\frac{4\pi}{q^2}).Img \mid \psi_0 > \widehat{P^\dagger}[E_i + \omega - \widehat{H_{eff}} + i\eta]^{-1}\hat{P} \mid \psi_0 > \quad \text{... (II.3)}$$

$$= \mu_0[1 + \sum_n \chi_n^l(\omega)] \quad \text{... (II.4)}$$

$$= \mu_0 \left[1 + \left[\sum_i (\chi_2)_{0i0} + \sum_{i\neq j} (\chi_3)_{oijo} + \sum_{i\neq j\neq k} (\chi_4)_{oijk} + \ldots\right]\right] \quad \text{... (II.5)}$$

The specific XAE XAFS spectral functions as normalized oscillatory function of HTSC with photoelectron MSP n originating and terminating at central photoabsorber

$$= \sum_n \chi_n^l(\omega) = \frac{\mu(\omega)-\mu_0(\omega)}{\Delta\mu_0} = \frac{\Delta\mu(\omega)}{\Delta\mu_0} = Img.Tr.(G_{sc})_{L,L'} \quad \text{... (II.6)}$$

$$= Img.s_0^2 \frac{e^{(\rho_1+\rho_2+\ldots\ldots+\rho_N+2\delta_l)}}{(\rho_1.\rho_2\ldots\ldots\ldots\rho_N)} Tr.M_{\alpha\beta}F_N F_{(N-1)} + \ldots . F_2.F_1 \quad \text{... (II.7)}$$

$$= \sum_{n\geq 2} \chi_n^l(\omega) + \sum_{n<2} \chi_n^l(\omega) \quad \text{... (II.8)}$$

XAS two-point response-function of interacting electrons [2]

$$\chi(r, r', \omega) = \chi_0(\omega) + \chi_0(\omega)\widehat{K}\chi(\omega) = [1 - \chi_0(\omega)\widehat{K}]^{-1}\chi_0(\omega) \quad \text{... (II.9)}$$

XAS response function for non-interacting electrons

$$\chi_0(\omega) = \sum_i f_i \psi_i^*(r)\psi_i(r)G(\vec{r}, r', E_i + \omega) \quad \text{... (II.10)}$$

The MS-matrix Kernel for photoexcited core-hole & local X-ray field interaction in TDDFT

$$\widehat{K} = G_0\widehat{t_l} = \delta(r - r')\frac{\delta V_{xc}(\rho)}{\delta\rho} = f_{xc}^{ALDA}(r_n r') \quad \text{... (II.11)}$$

with exchange correlation potential in adiabatic LDA (ALDA) of DFT

$$V_{xc}[\rho] = [\frac{3}{\pi}\rho(r)]^{\frac{1}{3}} \quad \text{.. (II.12)}$$

The dynamical photoelectron Green's function propagator $G(\vec{r}, r', E_i + \omega)$as Energy-resolvent operator in MSP

$$G(\vec{r}, r', \omega) = G_0 + G_0\widehat{T}G(r, r'\omega) \quad \text{... (II.13)}$$

with free photoelectron Green's function [1]:

$$G_0 = -2\vec{k}\sum_L R_L(r_<)H_L(r_>), \text{ with } R_L(r) = i^l R_l(r)Y_L(r) \quad \text{.. (II.14)}$$

The MSP Green's function [1] from electronic environment of atomic cluster around central atom

$$G_{sc}(r,r') = e^{i\delta_l}(1 - G_0\hat{t}_l)^{-1}G_0e^{i\delta_l} \quad \text{.. (II.15)}$$

The dynamical photoelectron MS-$\hat{t}$ metrix for MSP n from atoms of clustor

$$\hat{T} = \hat{t_i}\delta_{ji} + \hat{t_j}G_0\hat{t_i} + \sum_{k\neq i}\hat{t_j}\,G_0\hat{t_k}G_0\hat{t_i} = \hat{t_l}(I - G_0\hat{t_l})^{-1} \quad \text{.. (II.16)}$$

with MS t matrix as

$$\hat{t_l} = e^{i\delta_l}\sin\delta_l \quad \text{… (II.17)}$$

The dynamical photoelectric l- partial wave phase shifts:

$$\delta_l = -k\int_0^\infty r^2 j_l r(kr)V_{eff}d\vec{r} \quad \text{.. (II.18)}$$

The low photoelectron specific XAE XANES MS- resonances (MSR) spectral function of XAFS of HTSC's XAS

$$\sum_{n\geq 2}\chi_n^l(\omega) = \hat{T}[\frac{(t_0)_l}{\hat{T}(t_0)_l}.\frac{1}{(2l+1)}\sum_n\left(\Xi_{0i..j0}\right)_{LL}] \quad \text{.. (II.19)}$$

$$=[\sum_i(\chi_2)_{0i0} + \sum_{i\neq j}(\chi_3)_{0ij0} + \ldots..] \quad \text{.. (II.20)}$$

as n-particle distribution function with generic term ($\Xi_{0i..j0}$)

The high photoelectron energy specific XAE SS-EXAFS Spectral function of XAFS of HTSC's XAS

K-XAE SS-EXAFS Spectral Function of XAFS of HTSC XAS for MSP n=1

$$[\sum_{n<2}\chi_n^l(\omega)]_{K-XAE} = -\sum_j\frac{s_0^2N_jF_j(2k)}{kr^3}e^{-2kr_j}e^{-2r_j.\lambda_j}e^{-2\delta_j^2k^2}.sin\left[2kr_j + \delta_j\left((\omega) + \phi_j(k)\right)\right] \quad \text{.. (II.21)}$$

$$= -\sum_j\left[\frac{s_0^2N_j^l}{kr^3}e^{-2kr_j}\right]|F_j(k,\pi)|exp\left[-2(r_j).\lambda_j(k) - 2\sigma_j^2k^2 + C_{ei}\right]e^{-2r_j^2k/\lambda(k)}.sin\left[2kr_j + C_{oi}\right] \quad \text{.. (II.22)}$$

with MSRD DWF

$$C_{oi} = \frac{-4\pi\sigma_i^2k^2}{r_i}(1 + r_i/\lambda(k)) - \frac{4}{3}\sigma_l^{(3)}k^3 + \ldots + \ldots \quad \text{.. (II.23)}$$

$$C_{oi} = \frac{-4\pi\sigma_i^2k^2}{r_i}(1 + r_i/\lambda(k)) - \frac{4}{3}\sigma_l^{(3)}k^3 + \ldots, C_{ei} = \frac{2}{3}\sigma^{(4)}k^4 + \ldots \quad \text{.. (II.24)}$$

L-XAE SS-EXAFS spectral function of XAFS of HTSC's XAS

$$[\sum_{n<2}\chi_n^l(\omega)]_{LXAE} =$$
$$= \frac{\sum_j A_j(k)G'(r)[(1 - 3cos^2\theta)(1 < \psi_{l,2p}|\hat{z}|\psi_{l,s} >^2 sin(2kr_j + 2\delta_j(k))) + \frac{1}{2}(1 < \psi_{l,2p}|\hat{z}|\psi_{l,s} >|^2 sin(2kr_j + \delta_j k))]}{[|< \psi_{l,2p}|\hat{z}|\psi_{l,s}|^2 > + \frac{1}{2}\left\{|< \psi_{l,s}|\hat{z}|\psi'_{l,s}|^2 >\right\}]}$$

.. (II.25)

with notations have usual meanings [Stern in [1]].

The specific XAE XANES MSR and SS/MS-EXAFS of XAFS of HTSC's XAS [1,4] can be performed in combined LFTDDFT+BSE-RSGF approach with FEFF9 [3] computational SS/MS terms input which includes convergence of MS in SWA curvature effects, atomic scattering potential, dynamical photoelectron inelastic scattering energy losses, MPSE

self-energy shifts, Gaussian and Lorentzian thermal and static structural disorders as DWF $(\sigma_j)^2$ and many-body effects lumped into MPSE for screening of X ray field and screened core-hole-photoelectron interactions.

III. SUPERCONDUCTING DENSITY FUNCTIONAL THEORY (SCDFT) OF HTSC

The SCDFT formalisms [5-8] treats SC with these densities-normal and anomalous electron densities and diagonal of nuclear density matrix with a wide range of e-e interactions coupling. The Oliveira-Gross-Kohn (OGK) [5] SCDFT as the first step towards ab-initio theory of SC for weak e-e coupling. Recently, Kurth et.al. [6], Leuder et.al. [7] and Marques et.al. [8] developed SCDFT framework in which anomalous electron density called as SC order parameter appears as fundamental variable. The electron-phonon exchange interactions and Coulombic pseudo/retarded potential μ^* are treated on equal footings and the exchange correlational functional approximations are derived from many body perturbation theory. The basic Hohenberg-Kohn (HK) and Kohn-Sham (KS) theorems for SCDFT were proved by these theories and similar to simple harmonic oscillator describing the independent phononic modes and characterized electronic structures and SC properties- T_c, energy band gap Δ, SC order parameters, phononic modes and spectral function $\alpha^2F(\Omega)$ etc and these provides genesis of structural anisotropy of electronic state at fermi level E_F in Quantum ESPRESSO to explore sensitivity of T_c to RTSC parameterization in σ/π band states at fermi surface (FS) where the e-e electrostatics Coulombic repulsive force filed interactions pseudopotential (residual/retarded) actively acts differently in band states of HTSC stabilising the observed SC states and provide a genesis of structural anisotropy of electronic state at Fermi level (E_F) as orbital relaxation mechanism dominates over dipolar mechanisms and Fermi contacts mechanisms in HTSC. For SC, one of the most important parameters is the value of electronic density of states (DOS) at E_F, $N(E_F)$ in normal state, so the SCDFT formalisms for evaluation of $N(E_F)$ with represent an excellent probe to check not only DOS and its partial components but also characterization of electronic and atomic structures anisotropy distributions between in plane and out-of-plane states orbitals and validity of SCDFT in strong e-e coupling HTSC with estimation of SC parameters, revealing of Fermi surface (FS) sheets with different orbitals character (tubular structures with σ/π band) similar to e_{2g} phononic modes and corresponding to band-stretching in planes. Therefore, electronic and atomic structural and SC state characterization of HTSC with normalization effects in multiband with nonlinear, anharmonic e_2g optical phonic mechanism induced HTSC can be made by first principles SCDFT calculations of lattice dynamics in strong e-e coupling to electrons in tubular shaped sigma/pi bands at E_F in Quantum ESPRESSO [9] computer programme to explore sensitivity of T_c of HTSC to RTSC parameterization in σ/π bands at Fermi Surfaces (FS) and local field effects be in exchange correlation functionals of the theory.

The development of SCDFT be with followings:

Normal Electronic Density

$$n(r) = \sum_\sigma < \psi(r)^+_\sigma \widehat{\psi(r)^+_\sigma} > \quad \text{... (III.1)}$$

Anomalous Electronic Density

$$\chi(r, r') = \langle \widehat{\psi_\uparrow}(\vec{r})\psi_\downarrow(\vec{r}')\rangle \quad \text{... (III.2)}$$

Diagonal Part of Nuclear Density Matrix

$$\hat{\Gamma}(\vec{R}) = \widehat{\Phi^\dagger}(\overrightarrow{R_H})\widehat{\Phi}(\overrightarrow{R_N})\dots\widehat{\Phi}(\vec{R}) \quad \text{... (III.3)}$$

KS equation for electrons

$$[-\frac{\nabla^2}{2} + v_s^e(r) - \mu]u_i(r) + \int d^2\vec{r}'\Delta s(\vec{r}, \vec{r}')v_i(\vec{r}') = \widetilde{E}_\iota u_i \quad \text{... (III.4)}$$

KS equation for holes

$$-[-\frac{\nabla^2}{2} + v_s^e(r) - \mu]v_i(r) + \int d^3\vec{r}'\Delta s^*(\vec{r_\iota}, \vec{r}') = (i\omega') = \widetilde{E}_\iota u v_i(r) \quad \text{... (III.5)}$$

KS equation for nuclei (ions)

$$\left[-\sum_{\alpha}\frac{\nabla_{\alpha}^{2}}{2m}+v_{s}^{n}(\vec{R})\right]\Phi_{l}(\vec{R})=\varepsilon_{k}\bar{\Phi}(\vec{R}) \quad \text{... (III.6)}$$

HTSC Band-gap equation

$$\Delta_{i}=-Z_{i}|\mu|-\frac{1}{2}\sum_{j}K_{ij}\,|\mu|\frac{tanh\quad ij}{\zeta_{j}} \quad \text{... (III.7)}$$

HTSC's T_c Equation

$$T_{c}\propto\exp[\frac{1+Z(0)}{N(0)K(0)}]=\frac{\Omega\log}{1.20}\exp[\frac{-1.04(1+\lambda)}{\lambda-\mu^{*}(1+0.62\lambda)}] \quad \text{... (III.8)}$$

Taking strong e-e coupling Migdal-BCS-Eliashberg electron-phonon interaction phononic spectral function:

$$\alpha^{2}F(\Omega)=(Y_{N(0)})\sum\sum(g\Gamma_{i}'|\delta(\zeta_{i})|)\delta(\zeta_{j})\delta(\Omega-\Omega_{\lambda\zeta'}) \quad \text{... (III.9)}$$

IV. XAS AND SCDFT OF HTSC AB-INITIO CALCULATIONS

The combinations of LFT DDFT + BSE – RSGF-SWA formalism [2] of specific K/L XAE XANES IN FEFF9 [3] computational programme leading to efficient local electronic, atomic and morphological structural parameters of the intermetallic HTSC taking into account essential effects of e-e magnetic exchange interaction correlations, df/pd conduction band Jahn-Teller (BJT) structural distortion, and sensitivity of T_c as a function of dopant contents and level with active role of doped ions degrees of freedom in inter/intra-site/orbital planar couplings and SC phase transition of intermetallic HTSC at T_c approaching RTSC exploration. By using SCDFT formalism's [5-8] computer programme Quantum ESPRESSO [9] in the intermetallic HTSC's electronic structure and SC properties – T_c, energy band gap Δ_i , SC order parameter, phononic modes calculations give rise to characterization of HTSC [10,11] leading to RTSC as T_c is sensitive to isotropic dopant and supports strong e-e coupling phononic interaction mediated HTSC in which 2D/3D sigma/pi bands are filled with doping and giving structural anisotropy of electronic state at E_F or orbital relaxation dominates or dipolar and Fermi contact mechanisms. Therefore, an SCDFT formalism aspects of renormalized strong e-phonon exchange interaction induced HTSC in doped inter metallic HTSC phases leads to RTSC exploration with tubular structured FS sheets with sigma/pi band charters with non-linear anharmonic e_{2g} optical phononic modes induced HTSC.

V. CONCLUSIONS

The qualitative and quantitative characterization of intermetallic HTSC has been made with the performance of computations of specific XAE (K/L) XANES MSR and SS/MS EXAFS of XAS spectral features by using fast and efficient ab-initio computer package FEFF9 [3] of combined LFTD DFT+BSE-RSGF-SWA formalism [2] and SCDFT [5-8] package Quantum ESPRESSO [9]. These act as unique combination recently for possibility of T_c of HTSC [4,10,11] super lattice to reach RTSC parameterization with normalization effects in multi-bands with non-linear anharmonic e_{2g} optical phononic mechanism induced HTSC.

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