Density functional theory of phonon-driven superconductivity

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The success of density functional theory (DFT) for electronic structure calculations is at the basis of modern theoretical condensed matter physics. The original theorem of Hohenberg and Kohn (HK) and the reproducibility of the exact electronic density in a non-interacting Kohn Sham (KS) system both extend to, in principle, any electronic phase, including magnetism and superconductivity. However the practical applicability of KS-DFT depends on the availability of density functionals for the relevant observables of the system. As a matter of fact to derive density functionals able to describe the features of symmetry broken phases, in particular the order parameter (OP) of that phase, turns out to be a task of outstanding complexity.

A scheme to circumvent this problem is to generalize the HK theorem to include the OP as an additional density. The corresponding KS system then reproduces both the electronic and the additional density. In the case of superconductivity the original formulation of a DFT scheme (SCDFT) is due to Oliveira, Gross and Kohn[1] where the additional density is the order parameter of superconductivity $\chi(\mathbf{r}, \mathbf{r}') = \langle \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}')\rangle$. With a further development of DFT to include the nuclear degrees of freedom [2], in recent years an approximate exchange correlation potential F_{xc} for the KS Bogoliubov-de-Gennes system has been derived which features the electron-phonon (e-ph) and the electron-electron (e-e) interaction on the same footing [3].

This leads to a self-consistent equation for the superconducting OP that depends on the phononic features and on the normal-state electronic structure. In the space of single particle KS orbitals it is formally equivalent to a BCS gap equation

$$\Delta_{n\mathbf{k}} = \mathcal{Z}_{n\mathbf{k}}\Delta_{n\mathbf{k}} - \sum_{n'\mathbf{k}'}\mathcal{K}_{n'\mathbf{k}'}^{n\mathbf{k}}\frac{\tanh\left(\frac{\beta E_{n'\mathbf{k}'}}{2}\right)}{2E_{n'\mathbf{k}'}}\Delta_{n'\mathbf{k}'}, \tag{1}$$

where n and $\mathbf{k}$, respectively, are the electronic band index and the wave vector inside the Brillouin zone. β is the inverse temperature and $E_{n\mathbf{k}} = \sqrt{\xi_{n\mathbf{k}}^2 + |\Delta_{n\mathbf{k}}|^2}$ are the excitation energies of the KS system, defined in terms of the gap function $\Delta_{n\mathbf{k}}$ and the KS eigenvalues

$\xi_{n\mathbf{k}}$ measured with respect to the Fermi energy. The kernel, $\mathcal{K}$, consists of two contributions $\mathcal{K} = \mathcal{K}^{\text{e-ph}} + \mathcal{K}^{\text{e-e}}$, representing the effects of the e-ph and of the e-e interactions, respectively. The gap function is related to the the OP in the KS basis by $\chi_{n\mathbf{k}} = \frac{\Delta_{n\mathbf{k}}}{2E_{n\mathbf{k}}} \tanh\left(\frac{\beta}{2E_{n\mathbf{k}}}\right)$.

Compared to many-body perturbation theory, SCDFT features two major achievements: *1)* It is completely free of adjustable parameters. Coulomb and phonon mediated interactions are included without the need of introducing a phenomenological μ^*. *2)* all the frequency summations are performed analytically in the construction of F_{xc}. Retardation effects can be exactly included but at the same time the gap equation has still the form of a static BCS equation. The formal simplicity of Eq. 1 then allows to account for the anisotropy of real systems at a low computational cost.
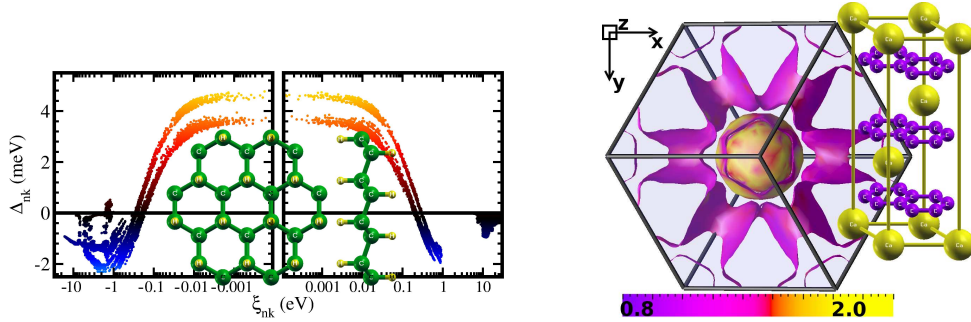

FIG. 1: Left: Superconducting gap of hole-doped graphane (hydrogenated graphene), as a function of the energy distance from the Fermi level. Right: the Superconducting gap of CaC_6, $n\mathbf{k}$-resolved on the Fermi Surface (the colorscale gives the SCDFT gap in meV).

At the Fermi energy ($\xi_{n\mathbf{k}} = 0$) the form of $\Delta_{n\mathbf{k}}$ is determined mostly by the attractive phononic term $\mathcal{K}^{\text{e-ph}}$. Beyond the phononic energy range the interaction becomes repulsive due the direct Coulomb interaction between electrons in $\mathcal{K}^{\text{e-e}}$. The system then maximizes its condensation energy by including a sign change in $\Delta_{n\mathbf{k}}$. In accordance with Eq. 1, when both the interaction and $\Delta_{n\mathbf{k}}$ change sign, then the overall contribution becomes once again attractive. This mechanism takes the name Coulomb renormalization.

The typical behavior of $\Delta_{n\mathbf{k}}$ versus $\xi_{n\mathbf{k}}$ is plotted in Fig. 1 for graphane (hydrogenated graphene C_2H_2). We use a logarithmic scale to enhance the behavior at the Fermi energy. This system shows a characteristic two gap structure, i.e. $\Delta_{n\mathbf{k}}$ at the Fermi energy shows two distinctly different values corresponding to the presence of two Fermi surfaces. A similar behaviour, but with three distinct gap values at the Fermi energy, is found for hydrogen under pressure. We predict that this material has a critical temperature of 242 K at 450

GPa[4].

The more anisotropic the Fermi surface and the electron-phonon coupling are the more structured becomes the gap function at the Fermi energy. An example is CaC_6 shown in Fig. 1 where the superconducting gap closely reflects the phononic anisotropy[5].

To go beyond this reciprocal space description, we have recently implemented a transformation of the superconducting OP $\chi_{n\mathbf{k}}$ back into real space.
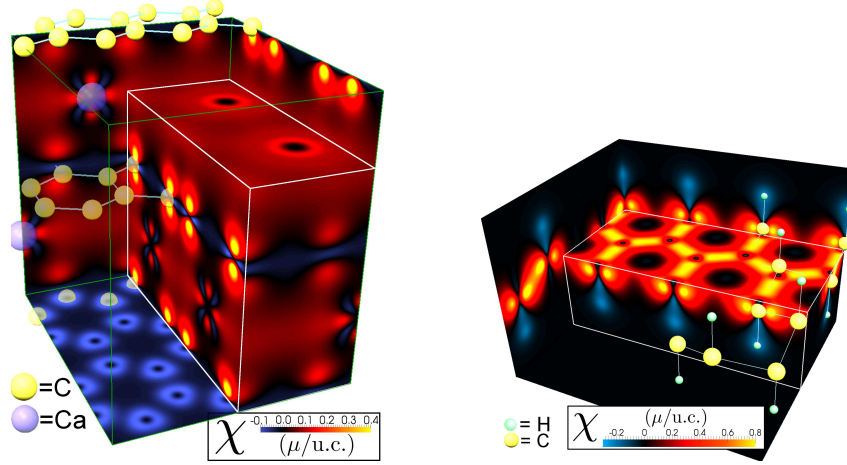

FIG. 2: $\chi(\mathbf{R}, \mathbf{0})$ of CaC_6 (left) and C_2H_2 (right)

This means to multiply the KS basis $\{\varphi_{n\mathbf{k}}(\mathbf{r})\}$ of the initial expansion:

$$\chi(\mathbf{R}, \mathbf{s}) = \sum_{n\mathbf{k}} \chi_{n\mathbf{k}} \varphi_{n\mathbf{k}}(\mathbf{r}) \varphi_{n\mathbf{k}}^*(\mathbf{r}') \tag{2}$$

where $\mathbf{R} = (\mathbf{r} + \mathbf{r}')/2$ and $\mathbf{s} = (\mathbf{r} - \mathbf{r}')$ are respectively the center of mass and the relative coordinate of the cooper pair. We are thereby able to connect the chemical bonding properties with superconducting features in a very graphic and compact way. As an example we show $\chi(\mathbf{R}, \mathbf{0})$ of CaC_6 and C_2H_2 in Fig. 2. The electronic bonds giving the largest contribution to superconductivity are clearly visible. In graphane the large positive values come from the sp^2 carbon bonds. In CaC_6 the dominant contribution arises from the π-states as well as d_{z^2} Ca orbitals and interlayer states. The Coulomb renormalization contributions is provided by the C-H bonds in graphane and by the sp^2 states of CaC_6 (blue regions).

Although this real space representation is formally equivalent to the reciprocal space one it results more natural when describing systems with large unit cells and complex geometries like surfaces. We have recently studied a lead monolayer deposited on the Si(111) surface. As shown in Fig. 3. From the real space description one can clearly appreciate the localization of the SC order parameter on the Pb layer, making this system a prototype for two dimensional
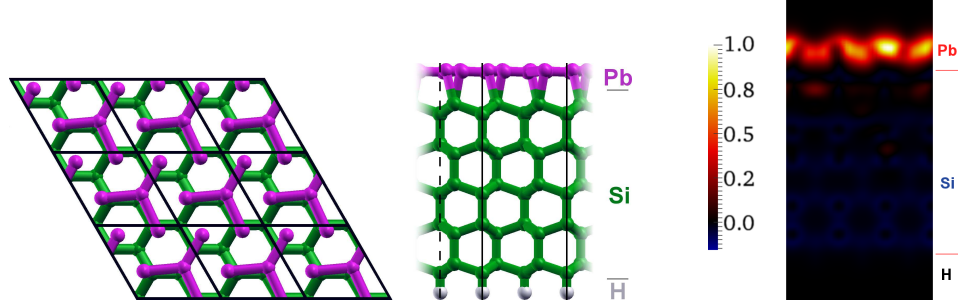
superconductivity.

FIG. 3: Crystal structure and SC order parameter for a Pb monolayer on the Si(111) surface. The lack of hybridization between lead and substrate makes the superconducting condensation extremely localized in real space.

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