

# Revisiting the Fermi Surface in Density Functional Theory

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**Abstract.** The Fermi surface is an abstract object in the reciprocal space of a crystal lattice, enclosing the set of all those electronic band states that are filled according to the Pauli principle. Its topology is dictated by the underlying lattice structure and its volume is the carrier density in the material. The Fermi surface is central to predictions of thermal, electrical, magnetic, optical and superconducting properties in metallic systems. Density functional theory is a first-principles method used to estimate the occupied-band energies and, in particular, the iso-energetic Fermi surface. In this review we survey several key facts about Fermi surfaces in complex systems, where a proper theoretical understanding is still lacking. We address some critical difficulties.

## 1. Introduction

Density Functional Theory (DFT) is the “model of choice” for understanding condensed matter at low energies. It has achieved a certain status as a standard first-principles method. Indeed for many, though not all, significant condensed-matter phenomena DFT is a powerful analytic tool for studying electronic, vibrational, magnetic, superconducting among others.

The basis of DFT (for example, see references [1]–[6]) rests upon two foundational theorems by Hohenberg and Kohn [7]. Over the last five decades great progress has been made on both the theory’s fundamental aspects and its scope in application to various systems. It has a reputation as one of the most successful practical methods for treating many-body systems on a fully quantum-mechanical footing.

In physical terms, however, it is many-body microscopics that ultimately fixes the complex solid-state properties one seeks to explain and predict. This essential many-body aspect is not addressed by DFT in any frontal way. Its approach to many-body interactions is an implicit, and thereby indirect, one by its positing certain well-defined but nevertheless approximate “exchange-correlation” (XC) forces between electron pairs.

The classic Kohn–Sham version of DFT [8] generates effectively single-particle simulations of what are, in actuality, interacting correlated multi-particle systems. The theory’s distinctive property is to recover, in principle, the real-space single-particle-number and energy densities of such a condensed system. Anything more than that cannot be inferred from the theorem, notably any phenomena involving excited states beyond the single-particle configuration. That is because such effects are irreducibly many-body in nature and, logically, demand an explicit many-body analysis.



To reinforce this fundamental point we recall the key physical reason why many-body mechanisms must, at some stage, appear explicitly in any description of interacting carriers. Landau, in his account of the weakly interacting Fermi liquid (see for instance Nozières and Pines [9]), showed that any energy change of an excited system away from the ground state takes the inevitable form

$$\delta E[f + \delta f] \equiv \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}[f] \delta f_{\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}'} F_{\mathbf{k}, \mathbf{k}'}[f] \delta f_{\mathbf{k}} \delta f_{\mathbf{k}'} \quad (1)$$

where  $f_{\mathbf{k}}$  is the single-particle-state distribution function, and  $\varepsilon_{\mathbf{k}}[f]$  is the corresponding single-particle spectrum in the interacting system. (The more general Landau formula describes the interacting free energy at finite temperature  $T$ ; in this case  $\delta f$  may as readily represent the effect of a thermal energy change, that is away from  $T = 0$ , as that of any other perturbation; a situation on which we have much more to say in the following.) Crucially, Landau's two-particle interaction potential  $F_{\mathbf{k}, \mathbf{k}'}[f]$  appears in equation (1). Such an interaction is not representable by *any* single-particle functional.

Although DFT, in principle, does guarantee replication of the exact total ground-state energy  $E[f]$  over the occupied single-particle states, it cannot guarantee

(a) that its effective single-particle spectrum, say  $\{\tilde{\varepsilon}_{\mathbf{k}}[n]\}_{\mathbf{k}}$ , as an auxiliary functional of the real-space density  $n(\mathbf{r})$ , is literally the replica of the actual one  $\{\varepsilon_{\mathbf{k}}[f]\}_{\mathbf{k}}$ , and

(b) that it will furnish a systematic estimate for the interaction potential.

Both (a) and (b) are essential to a description of the full behaviour of the particle assembly. For example, the physical response of the real system to any perturbation in the single-particle distribution is characterised directly by

$$\chi_{\mathbf{k}, \mathbf{k}'}[f] \equiv \frac{\delta^2 E}{\delta f_{\mathbf{k}} \delta f_{\mathbf{k}'}} \equiv F_{\mathbf{k}, \mathbf{k}'}[f].$$

Consequently the so-called Landau interaction parameters  $F$  mediate, directly, all essential properties such as the dielectric response, spin susceptibility, compressibility, specific heat, and so on [9].

As we have remarked, the interaction parameters are inherently two-body properties that cannot be simulated merely in single-particle terms. This means that density functional theory for the ground state alone, viewed as the definitive and optimal *strictly single-particle* description of a many-body system, is insufficient to capture many significant response properties of a real, correlated system. Yet it is the response of a system over the entire arsenal of experimental probes that provides the structural information one needs to discover.

The inbuilt limitations of the Kohn–Sham formalism are inherited by any and all DFT-based machinery relying upon it exclusively. Owing to the essentially noninteracting, single-particle nature of the resultant models (and notwithstanding the popularity of DFT as a practical tool applied to actual many-body problems), a basic question of physics remains to be answered: How can one bring to experimental test any differences (at the very least, in the ground-state properties) between DFT as an effective one-body theory, and the established canon of many-body analysis?

In testing the limits of DFT the detailed measurable properties of the Fermi surface are particularly relevant. At the best of times, these are delicate qualities to predict. A widespread assumption still goes largely unquestioned: namely, that the Fermi surface, with all of its intricate topology, is uniquely a ground-state property and, uniquely, determinable via DFT. This cannot be the case in general, least of all for the complex interacting structures of current interest.

For ideal free carriers in an ideally uniform three-dimensional sample, the Fermi sphere is bounded by an equi-energetic surface of constant curvature, of radius  $k_F$ , the Fermi momentum. Luttinger and Ward [10] showed that, in such a uniform metallic system, the Fermi surface will survive in the presence of inter-particle interactions. All of the low-lying excitations of the system live near the Fermi surface and account for much of the system's low-temperature behaviour.

Nevertheless, the real Fermi surfaces of real materials are not simply spheres or even quasi-spheres of at least positive curvature everywhere. Indeed they are topologically complicated, often multiply connected, and highly subject to the underlying crystalline geometry and interactions. They can even come as disconnected Fermi-surface pieces, as well as exhibiting Fermi-surface "nesting". The latter can induce unusual instabilities in certain metals: for example, at sufficiently low temperature a normal metal may move into a charge- or spin-density-wave state or other topological phase transition.

Present condensed-state research must deal extensively with novel and exotic materials. Invariably these are moderately to highly correlated in terms of their strong collective electron interactions. It follows that the relevant physics will necessarily display its many-body nature [11]-[13]. Equally it follows, in this context, that attempts to use any single-body description must be weighed with care.

In the next Section we outline the basic features of density functional theory. In view of very large growth in literature we present a brief picture of it, keeping only the salient points for our purpose. We discuss which ground-state properties within DFT can be trusted to give a reliable physical estimate, as well as what it is not designed to address. In Sec. 3 we survey various popular approximations to model the exchange-correlation functional, and present their relative merits or demerits. In this Section we provide a list of the most often-used computer codes that DFT practitioners rely upon.

In Sec. 4 we revisit a basic open question, still unresolved today: Is the Fermi surface uniquely a one-body ground-state property? From a many-body perspective this question has to be addressed carefully at zero temperature. Experimental observation of the Fermi surfaces from angle-resolved photo-emission spectroscopy (ARPES), Kohn anomaly, Shubnikov-de Haas and angle resolved magneto-resistance (ARMR) methods are discussed briefly and contrasted with calculated results of DFT, quasi-particle (GW) theory and DMFT. In Sec 5 finite-temperature aspects are discussed, since all actual experiments are done at  $T > 0$ . Our Summary with conclusions is presented in the final Section.

## 2. Outline of DFT

### 2.1. Hohenberg-Kohn theorem

The Theorem for the Energy Functional of Hohenberg and Kohn [7] (an existence proof) states the following. Admitting certain general assumptions, any change in the ground-state density  $n(\mathbf{r})$  of an interacting electron system subject to an adiabatically changing external potential  $v_{\text{ext}}(\mathbf{r})$ , remains in one-to-one correspondence with that potential.

Since both  $n(\mathbf{r})$  and the total number of particles,  $N$ , are uniquely tied to  $v_{\text{ext}}$  we can readily construct the full system Hamiltonian. From it,  $n(\mathbf{r})$  can be calculated by solving a Schrödinger-like equation derived from a variational principle. We skip the many technical details (see references [1]-[6]) and proceed the popular Kohn-Sham method [8].

The total energy is given as a functional of the spatial density distribution  $n(\mathbf{r})$  by

$$E[n] = T[n] + U[n] + V_{\text{ext}}[n] = T[n] + U[n] + \int n(\mathbf{r})v_{\text{ext}}(\mathbf{r})d\mathbf{r}, \quad (2)$$

in which the first two terms on the right-hand side are the total kinetic energy  $T$  and total inter-particle interaction energy  $U$ . The total potential energy  $V_{\text{ext}}$  includes the electron-ion

electrostatic interaction, here considered to be external to the system of mobile electrons.

In the Kohn-Sham (KS) method we consider the kinetic energy to be exactly equivalent to that of a system of independent (noninteracting) electrons, with a basis of single-particle orbitals  $\{\phi_i[n]\}_{i=1}^N$  that are themselves functionals of the exact density distribution for the  $N$  electrons in the ground state of the system. The theorem guarantees these orbitals to be well-defined. They are determined systematically, in a self-consistent fashion.

The fundamental expression from the DFT analysis of the total ground-state energy now becomes more explicit in detail. In this setting we have

$$E[n] \equiv T[\phi_i] + U_H[\phi_i] + E_{xc}[\phi_i] + V_{\text{ext}}[\phi_i]; \quad (3)$$

the interaction energy  $U$  is first resolved into the mean-field Hartree component  $U_H$  and the exchange-correlation component  $E_{xc}$  with

$$U_H[\phi_i] = \frac{1}{2} \int d\mathbf{r} v_H(\mathbf{r}) n(\mathbf{r}).$$

The set of orbitals is obtained through the Kohn-Sham equations (here indexed by the Brillouin-zone wavevector  $\mathbf{k}$ ):

$$\begin{aligned} \left[ \frac{\hbar^2 k^2}{2m} + v_{\text{eff}}(\mathbf{r}) \right] \phi_{\mathbf{k}}(\mathbf{r}) &= \tilde{\varepsilon}_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r}), \quad \text{where} \\ v_{\text{eff}}(\mathbf{r}) &\equiv v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}), \quad \text{with} \\ v_H(\mathbf{r}) &= \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' n(\mathbf{r}'), \quad \text{and} \quad v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \end{aligned} \quad (4)$$

Two final steps are required to close this system self-consistently. First we define the constitutive relation for the density in terms of the single-particle KS orbitals:

$$n(\mathbf{r}) \equiv \sum_{\mathbf{k}} \theta(\mathbf{k}) |\phi_{\mathbf{k}}[n(\mathbf{r})]|^2 \quad (5)$$

writing  $\theta(k) = \theta(\tilde{\varepsilon}_F - \tilde{\varepsilon}_{\mathbf{k}})$  for the carrier occupation number, equal to unity within the occupied Fermi sphere and zero for the empty momentum states  $\mathbf{k}$  above it; here  $\tilde{\varepsilon}_F$  is the corresponding DFT estimate of the Fermi energy. Second, an explicit form has to be decided for the exchange-correlation functional  $E_{xc}[\phi_i]$  so that  $v_{xc}$  can be constructed and fed into the KS equations. We defer this crucial point of principle to section 3.1 below.

By varying the total energy with respect to the undetermined orbitals  $\phi_{\mathbf{k}}$  we obtain the  $N$  Euler-Lagrange equations for the system. They are coupled nonlinear Schrödinger-orbital equations, conceptually very similar to Hartree-Fock but containing much more correlational input, over and above exchange.

The volume of  $k$ -space, enclosed by the Fermi iso-surface defined as  $\{\mathbf{k}; \tilde{\varepsilon}_{\mathbf{k}} = \tilde{\varepsilon}_F\}$ , is exactly the number  $N$  of mobile electrons physically occupying the lowest-lying states within the sample. Conservation of carriers requires this to be an invariant property of the closed system. In particular, any imposed external field may distort the surface and even change its topology substantially, but cannot alter the enclosed volume except possibly in a phase transition that totally re-orders the ground state.

## 2.2. Meaning of the Kohn-Sham eigenenergies

Just as with Hartree-Fock theory, the early precursor of DFT, the total energy  $E[n]$  is not the sum of all the single-carrier orbital energies  $\tilde{\epsilon}_{\mathbf{k}}$ . In fact, we know from the derivation that the  $\tilde{\epsilon}_{\mathbf{k}}$  enter purely as Lagrange multipliers; variational parameters that are strictly artifacts from the physical standpoint. The set of  $\tilde{\epsilon}_{\mathbf{k}}$  is simply the set of formal eigenvalues for the auxiliary one-body equations of DFT, whose eigenfunctions are guaranteed only to yield the correct local density  $n(\mathbf{r})$ ; nothing else.

It is the net density profile, not its auxiliary contributions, that carries the genuine physical content of the KS equations. While the auxiliary KS eigenvalues may generally bear some qualitative resemblance to the true energy spectrum, there exists no guarantee that they form a trustworthy representation of the true single-particle spectrum.

There is one important exception to the caveat above. The value for the DFT Fermi energy  $\tilde{\epsilon}_{\text{F}}$  is, at least in principle, the actual Fermi level in the ground state. But this does not mean that the microscopic *topology* of the Fermi surface is at all reproduced by DFT.

We stress that, although there may be practical and even heuristic reasons to suggest that the set  $\{\tilde{\epsilon}_{\mathbf{k}}\}_{\mathbf{k}}$  describes the “true” band structure, to date a basic microscopic justification of this hypothesis remains anything but settled. See for example references [14]-[16].

## 3. Implementation of the Kohn-Sham formulation

The only quantity that remains to be fixed is  $E_{\text{xc}}[n]$ , the exchange–correlation energy functional. It is formally defined by the adiabatic connection formula [2], [5]. For computation, the expression for  $E_{\text{xc}}[n]$  has to be carefully constructed. This is where great efforts have gone into constructing several approximate expressions, namely the so-called LDA, GEA, GGA, hybrid functionals, ODF, and so on [4]-[6]. We now outline their main characteristics.

### 3.1. Approximations for the density functional

(a) Local-Density Approximation (LDA): the general strategy of local-density approximations, as also those for local-spin-density (LSD) is to take known results for the XC potential  $v_{\text{xc}}[\nu]$  of a uniform system at density  $\nu$  and apply them locally to an inhomogeneous system. This, in this model,  $E_{\text{xc}}[n(\mathbf{r})]$  becomes a sum of locally homogeneous (possibly spin-dependent) exchange–correlation energies of electrons over a small cell in real space, with a homogeneous density  $\nu$  matching the local value  $n(\mathbf{r})$ .

Given this Ansatz, the total XC energy is approximated as

$$E_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) v_{\text{xc}}[n(\mathbf{r})]; \quad v_{\text{xc}}[\nu] \equiv \frac{\delta E_{\text{xc}}[\nu]}{\delta \nu}.$$

This formula works well when density gradients are small over the typical range of  $k_{\text{F}}(r)^{-1}$ , the Fermi wavelength. Forms for  $E_{\text{xc}}[n]$  in LDA are often taken from parametrisation of highly precise Quantum Monte Carlo (QMC) calculations for the electron liquid.

(b) Gradient-Expansion Approximation (GEA): If the density variation is not small, one can try to include systematically the gradient corrections to the LDA expressions, going as  $|n(\mathbf{r})|$ ,  $|n(\mathbf{r})|^2$ , etc.. In practice, low-order gradient corrections almost never improve the LDA results and higher-order corrections are exceedingly difficult to calculate. In any case, for real systems the results of GEA are worse than those of LDA [2].

(c) Generalised Gradient Approximation (GGA): Instead of finite-order, power-series-like gradient expansions one can use more general functionals of  $n(\mathbf{r})$  and  $\nabla n(\mathbf{r})$ , which need not proceed order by order. Such functionals assume the general form

$$E_{\text{xc}}^{\text{GGA}}[n] = \int d\mathbf{r} f(n(\mathbf{r}); \nabla n(\mathbf{r})) n(\mathbf{r}),$$

where the  $f(n(\mathbf{r}), \nabla n(\mathbf{r}))$ , now non-local, is carefully constructed by satisfying at least the leading conservation sum-rules such as perfect-screening (of each carrier by its exchange-correlation hole). Various fitted forms are available in the current literature [6].

(d) Hybrid functionals: These form a set of approximate forms for the exchange-correlation energies, incorporating a portion of the exact exchange term via Kohn-Sham wave functions together with correlation estimates from empirical sources.

There are many parametrised hybrid forms, some of which are of use in atomic and molecular calculations. One of the forms is given here:

$$E_{xc}^{\text{hybrid}} \equiv aE_x^{\text{exact}} + (1 - a)E_x^{\text{GGA}} + E_c^{\text{GGA}},$$

where  $a$  is an adjustable mixing coefficient.

(e) Orbital-dependent functionals: This is known as the “third generation” of DFT. For details, see Engels’ paper in chapter 2 of reference [2]. Here, instead of just density-dependent functionals, one uses orbital-dependent functionals. Since the orbitals will obviously embody more microscopic information, there are several advantages of this approach to highly correlated systems.

(f) Calculations by a sort of garden variety of techniques: these apply both to the methodology and to functional approximations too numerous to detail here: the so-called VASP, SIESTA, CRYSTAL, PAW, CASTEP, Quantum Espresso, FPLO, ABNIT. And so on. Some of these functionals have been devised for building into computer codes developed over many years by many people. These codes opened many new gates to the detailed computation of many physical quantities and were popularly adopted by large numbers of practitioners, even when the quantities calculated were being pushed somewhat beyond the advertised “fitness-for-use” of the codes.

### 3.2. Successes and failures

It is difficult to describe in simple terms not only the noted successes of DFT but also, more to the point, the sometimes minimised cases of its failures. There are many reviews and texts to highlight fulsomely its manifold impressive successes.

Regarding the alleged outstanding success of the GGA, Perdew and Kurth [2] have written that “LSD has been so successful in SSP [solid state physics] and a small residue of GGA nonlocality in solids does *not* provide a universally better description than LSD.”

Kokko and Das [17] have shown LDA and GGA do not always afford regular systematics, making it difficult to say objectively which one is better for ground-state properties of inhomogeneous systems, such as 3d and 4d transition metals. Many discussions have appeared in the past few years regarding the successes and failures of these DFT approximations [4], [6], [18]. The general belief seems to be that the approximations are systematically developed, despite their remaining always somewhat uncontrolled and therefore placing their reliability in question.

## 4. Fermi surfaces of metals

In keeping with the central issue of this paper, at this stage we are able to discuss questions on the nature of Fermi surfaces and the adequacy of their description.

### 4.1. Is the Fermi surface of a metal a ground-state property?

It is widely held that the set of iso-energetic electron bands crossing the Fermi level  $\epsilon_F$  define the Fermi surface (FS); a key quantity in understanding the electronic structure of any metallic material. This simple intersection may fix the true locus of the FS, or it may not (depending on

how faithful is the model). But it certainly tells nothing of the physical properties, qualitative and quantitative over the entire surface itself.

The conventional way of mapping a Fermi surface is to measure the energy-distribution curves (EDC), for distinct  $k$ -points of the Brillouin zone, via angle-resolved photoemission spectroscopy (ARPES) and thus to ascertain the  $k$ -locations where the bands transect the Fermi energy. The connection between band structure and ARPES results is authoritatively discussed in references [19] (an especially clear review of ARPES techniques) and [20].

The main issue is that a metal hosting many-electron correlations will retain a well-defined Fermi surface. In relatively weakly correlated metals, the single-electron (i.e. independent-particle) band structure reproduces the measured FS reasonably faithfully. As mentioned before, certainly for strongly correlated systems and even when strongly correlated, the one-electron band structure is liable to become inadequate in providing a good picture of the FS. From equation (2) the introduction we recall the need to compute at least the two-body Landau interaction  $F_{\mathbf{k},\mathbf{k}'}$  at the Fermi surface to determine the response properties.

It is then clearly necessary to check the results of the single-particle DFT for both band structure and the energy dispersion of the quasi-particle (that is, many-body-dominated) energies. In the Fermi-liquid picture, absent any inter-particle interactions, the band distribution of the carriers at  $T = 0$  is the Fermi-Dirac step  $f_{\mathbf{k}} = \theta(\varepsilon_{\mathbf{F}} - \varepsilon_{\mathbf{k}})$ . This noninteracting distribution is precisely the formal situation required within KS theory.

By contrast, in the presence of interactions the would-be step function, even at zero temperature, becomes smeared around the Fermi energy. This is because minimisation of the total interacting ground-state energy favours a physical configuration in which a portion of the (otherwise noninteracting) one-body excitations is relocated in  $k$ -space from somewhat below to somewhat above the Fermi level. In other words: an increase of kinetic energy for the distribution, by promotion of lower-lying electrons to slightly higher states, is more than offset by a lowering of the collective correlation energy.

Owing to this interaction-induced rearrangement, the originally noninteracting single-particle modes about the FS map one-to-one to stable (but now correlated) quasi-particle (QP) state counterparts, whose distribution retains the step-function form. But within the noninteracting-basis picture, this induces the appearance of a renormalisation constant  $Z_k$  at the Fermi surface;  $Z_k$  is always less than unity and rescales the jump in occupancy of the underlying *non-interacting* states at the Fermi level. Its size is fixed by the self-energy correction at the FS, arising from the many-body correlation effects.

The self-energy is immediately related to the Landau two-particle interaction [9] and therefore cannot be extracted from a purely one-body analysis. For, while the knowledge of the particle-particle interaction is sufficient to determine the self-energy and thus its contribution to the (true) band spectrum  $\varepsilon_{\mathbf{k}}$ , any model spectrum  $\tilde{\varepsilon}_{\mathbf{k}}$  is not in itself sufficient to determine the interaction. That is the core difficulty in securing the adequacy of DFT to describe the Fermi-surface reconstitution, or “renormalisation”.

We arrive at a crucial point. In its many-body setting, when described relative to the originally noninteracting single-particle basis, the Fermi surface is always “renormalised” by contributions that are explicitly many-body in nature. The FS is deformed away from its noninteracting profile depending on the strength of interaction. This highlights the central fact that the physical ground state need not at all conform to the intuitive picture provided by effective one-body formulations such as DFT or by its conceptual ancestor, Hartree-Fock.

For simple bulk metals the Fermi temperature  $T_{\mathbf{F}} = \varepsilon_{\mathbf{F}}/k_{\mathbf{B}}$  can be large, on the order of  $10^4\text{K}$  and more. There, it is a good approximation to treat the distribution  $f_{\mathbf{k}}$  in its zero- $T$  limit; namely, a step function with cut-off at  $\varepsilon_{\mathbf{F}}$ . However, for complex metals possessing various phase transitions at low temperatures, the  $T = 0$  limiting approximation will be of no use in capturing the correct physics. That is because the interactions themselves, quite apart from any thermal

effects, have already smeared it out.

Even when phase transitions are not in play, we have seen how many-body renormalisation can induce a radical change in the landscape of the critical states around a “normal” Fermi surface. In the potential presence of phase changes, one has even less option than to approach head-on the theory of finite-temperature effects on electronic structure. The quick fix does not exist here.

Energy bands as estimated by DFT differ substantially from the actual QP states described by many-body theory. This is evident when comparing the respective DFT and QP expressions

$$\begin{aligned} \left[ \frac{\hbar^2}{2m} k^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \phi_{\mathbf{k}}(\mathbf{r}) &= \tilde{\varepsilon}_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r}); \\ \left[ \frac{\hbar^2}{2m} k^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{\mathbf{k}}) \psi_{\mathbf{k}}(\mathbf{r}') &= \varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}). \end{aligned} \quad (6)$$

In the latter expression arising from standard many-body analysis,  $\Sigma(\mathbf{r}, \mathbf{r}'; \omega)$  is the nonlocal, irreducible electronic self-energy. This dynamical self-energy term is far more structured and internally complex than its static DFT analogue  $v_{\text{xc}}$ .

There exists a wide range of systematic and consistent approximations for  $\Sigma$ . A relatively simple and successful such model is the “GW” approximation, in which the “G” stands for the one-body Green function and the “W” for the microscopically screened two-body interaction [21]. In the frequency domain  $\Sigma(\mathbf{r}, \mathbf{r}'; \omega)$  is given by

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) \equiv i \int d\omega' G(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}', \mathbf{r}; \omega'),$$

in which the screened electron-electron interaction is approximated by

$$W(\mathbf{r}', \mathbf{r}; \omega') \equiv \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}', \mathbf{r}''; \omega) v(\mathbf{r}'' - \mathbf{r}).$$

and here  $\epsilon^{-1}(\mathbf{r}', \mathbf{r}''; \omega)$  is the inverse of the dynamic dielectric function.

If  $v_{\text{xc}}$  were a good approximation to  $\Sigma$  the DFT band energies  $\tilde{\varepsilon}_{\mathbf{k}}$  would also be good. However, comparison of calculations performed within KS and GW show large differences near the Fermi wave vector. There are many examples of DFT Fermi surfaces which are manifestly at variance with the physical, many-body QP Fermi surface. This is particularly so in multi-band and correlated materials [22], [23].

#### 4.2. Fermi surfaces from dynamical mean-field theory

Dynamical mean-field theory (DMFT) is a new development that takes into account local correlations more faithfully [24]. It is an improved GW method, where local correlations are incorporated by treating them as effective impurities in a periodic system. In brief, the method produces an effective mass and the associated renormalisation for the QPs can be a substantial, consistent with observed ARPES [25] in correlated electron systems.

#### 4.3. Is the DFT-Kohn-Sham Fermi surface a ground-state property?

At the start of this Section we examined the wider issues of principle leading to this question. The answer is straightforward. The KS equations certainly reproduce the correct physical density distribution and the total ground-state energy. In the course of things, given that a band structure emerges out of KS, a FS must also exist for it.

Nevertheless, when it comes to real systems with their interactions and inhomogeneities, the FS of DFT-KS is already known to be inequivalent *in principle* to the physical FS obtained from the microscopic Dyson equation [26], [27], which codifies the many-body effects within the true QP distribution. A detailed theoretical argument demonstrates that the inaccuracy of the FS in DFT-KS theory comes from an inbuilt lack of sufficiently strict convergence for the gradient approximation implicit in DFT.

In an analysis using a time-dependent generalisation of DFT, Cohen and Wasserman [28] conclude that KS FS is identical to the QP FS in the sense of a “distributional” argument – that is, at best in some average sense.

#### 4.4. Are explicit many-body effects seen in the FS properties of metals?

We cite some apposite and fruitful observations on the issue.

- A.K. Rajagopal notes in his review [14]: “The eigenvalues [of the DFT equation] do not have any special significance. The equation is a mathematical artifact of the HKS [Hohenberg-Kohn-Sham] formalism. By taking a pragmatic point of view by treating  $E_i$  [our  $\tilde{\epsilon}_{\mathbf{k}}$ ] as a one electron eigenvalue in the one electron theory of band structure, one arrives at the HKS band structure. There is much controversy regarding the definition of “Fermi surface” whether it is a ground state property of the system or not?”
- Richard Martin, on p. 131 of his text [15], also visits this point. We quote: “Is the exact Fermi surface of a metal given by the exact ground state DFT? .... this is not a trivial question for two reasons (i) a many-body metal must have a well-defined FS - this is assumed for the purpose. (ii) It is not a-priori obvious that FS is a ground state property. One way to see if the FS is determined by a ground state property is to consider the susceptibility to static perturbations. The exact DFT must lead to the correct Kohn anomaly and Friedel oscillations of the density far from an impurity, which depend in detail on the shape of the FS of the unperturbed metal.”

We return to Martin’s last point in detail, in subsection 4.7 below; since a singularity in the dielectric susceptibility  $\chi(q)$  is induced by electron-hole FS excitations when  $q = 2k_F$  spans the Fermi surface (the Kohn anomaly), one may reconstruct the physical FS from this information. The loci of the singularity trace out the FS. It is thus natural, and appropriate, to interrogate the effectiveness of DFT-based approaches as to how well their FS estimates match measured singularity data.

#### 4.5. Instability of the Fermi surface

If the FS is a robust ground-state property, exactly how stable is it against perturbations? Here are several examples.

- For a number of reasons including interactions, temperature and impurities, a system of metallic electrons can undergo a phase transition precipitated by superconducting or magnetic pairing; by a charge- or spin-density wave (CDW/SDW); by a nematic state; or a number of other many-body collective states.
- As mentioned in the Introduction, Landau’s theory of the Fermi liquid of 1957 became the canonical description of the metallic state. It was realised, even at that time, that the FS is unstable against strong interactions; the Pomeranchuk instability. A simple example occurs when an initially isotropic FS loses its symmetry in the presence of a strong interaction. The system will minimise its free energy at the cost of the FS becoming distorted and anisotropic. Again, the gain in kinetic energy is more than offset by a lowering of correlation energy.

- During the past few years a number of models in 2D systems have been studied, both theoretically and experimentally. These have once more brought to the fore important questions in our understanding of the FS as an invariant ground-state property [29]–[34].

#### 4.6. How does one determine the FS?

A good exposition of Fermi-surface analysis is given in the text by Ziman [34]. Currently one can try to map out the FS by the following means:

(i) Theoretically, by DFT through the naive KS band structure (with formally questionable status).

(ii) DFT augmented with *exact* response theory.

(iii) Empirically, by ARPES [19], [20] measurements: the ARPES spectrum is not just a set of one-electron bands, but measures directly quasi-particle spectral function  $A(\mathbf{k}, \omega)$ , given theoretically by the imaginary part of the Green function for one-particle excitations, with interaction effects (self-energy) fully included:

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im}\{G(\mathbf{k}, \omega)\} = -\frac{1}{\pi} \text{Im}\left\{ \frac{1}{\hbar\omega - \varepsilon_{\mathbf{k}}^0 - \Sigma(\mathbf{k}, \omega)} \right\}$$

where  $\varepsilon_{\mathbf{k}}^0$  is the noninteracting single-carrier energy and  $\Sigma(\mathbf{k}, \omega)$  can be calculated by GW or DMFT.

(iv) Magnetic resonance effects. Electronic Fermi surfaces are selectively measured by observing of the oscillation of transport properties in differently oriented magnetic fields  $\mathbf{H}$ . This approach results in, for example, the de Haas–van Alphen effect (dHvA) and the Shubnikov–de Haas effect (SdH). The former is an oscillation in magnetic susceptibility and the latter in resistivity. The determination of the periods of oscillation for various strengths and directions of  $\mathbf{H}$  allows one to infer the size and shape of the Fermi surface [34].

(v) Mapping out the FS using Angle-Dependent Magneto-Resistance oscillations (ADMRO) [36], [37]. Reference [36] has a comparison of ARPES and the ADMRO measurements in  $\text{Sr}_2\text{RuO}_4$ . The authors point out certain obvious inconsistencies in the ARPES data.

#### 4.7. Fermi surface from canonical response theory

The Lindhard formula for the charge-density response (see reference [34], p 129) is defined for noninteracting electron states, with occupancy  $f_{\mathbf{k}}^0$  at band energy  $\varepsilon_{\mathbf{k}}^0$ . The dielectric function  $\epsilon(\mathbf{q}, \omega)$  of an electron liquid is then given by

$$\epsilon(\mathbf{q}, \omega) = 1 - v(q)\chi(\mathbf{q}, \omega) \quad \text{where} \quad \chi(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q}}^0 - f_{\mathbf{k}}^0}{\hbar\omega - \varepsilon_{\mathbf{k}+\mathbf{q}}^0 + \varepsilon_{\mathbf{k}}^0}. \quad (7)$$

Evaluating this quantity and taking its static limit  $\omega \rightarrow 0$  at finite  $q$  and  $T = 0$ , we have

$$\chi(\mathbf{q}) \equiv \chi(\mathbf{q}, 0) = \frac{3n}{4\varepsilon_F} \left[ 1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (8)$$

This formula is logarithmically singular at  $q = 2k_F$ .

The dielectric function is continuous but its  $q$ -derivative has a logarithmic infinity at  $q = 2k_F$ . A more realistic calculation shows that the singular logarithmic behaviour is not only evident in the static dielectric susceptibility for an isotropic FS, but indeed that the logarithmic anomaly occurs for any Fermi surface, where  $\chi(\mathbf{q}, \omega)$  assumes the quite general form displayed in the second of the expressions given in equation (7).

The Kohn singularity will manifest itself under very broad conditions. It demands only that there be a non-vanishing iso-energetic Fermi surface. If one selects a measurement with  $\mathbf{q} = 2\mathbf{k}$

as a function of orientation for those Fermi momenta spanning the Fermi surface (that is, such that  $\varepsilon_{\mathbf{k}} = \varepsilon_F$ ) one maps out the physical FS in reciprocal space.

For a lattice system the inter-ionic potential is quasi-statically screened by the dielectric function. As a result the phonon frequency, which is much lower than the Fermi energy, is itself dependent on  $\epsilon(\mathbf{q}) = 1 - v(q)\chi(\mathbf{q})$ . Thus the singularity is reflected as a distinct “kink” in the phonon dispersion, known as the Kohn anomaly [38].

The dynamic dielectric function  $\epsilon(\mathbf{q}, \omega)$  can be constructed from detailed many-body theory by systematic inclusion of the exchange-correlation forces. In this context two theories are at hand: (1) the Kohn-Sham theory of independent electrons (subsuming all many-body effects into an effective one-body potential) and (2) explicit many-body terms contributing directly to the Dyson equation for the quasi-particle excitations. One can then very well see that the Kohn singularity appears in both KS and QP Fermi surfaces, since both approaches lead to a well-defined estimate for it. They may then be compared as to their agreement with the Kohn-anomaly phonon data, among others.

## 5. Finite-temperature effects on the FS

DFT was formally extended by Mermin [37] to include finite temperatures, by considering a grand canonical ensemble of particles. Unlike the case of the theory for  $T = 0$ , no rigorous DFT functional is available for the grand potential. Nevertheless there are some approximate LDA-type functionals that have been invoked in plasma physics, nuclear physics and quantum-chemistry applications of DFT [39].

To our knowledge, finite-temperature band structures are rarely considered relevant to metal physics. This is understandable for simple metals, since the Fermi temperature far exceeds the scale of any experimental  $T$ . The electronic structure and FS at room temperature and below are reasonably well understood, taking into account the constraints previously discussed. Further, these systems do not exhibit any phase change at low temperatures. Here, therefore, one believes that  $T = 0$  DFT is adequate and there are many calculations reported in the literature.

In reference [40] a calculation by the LDA+DMFT method is compared with ARPES and dHvA experimental results. It is shown there that DFT calculations, either with LDA or GGA, fail to reproduce the experimentally observed electronic structure of the multi-band material  $\text{KFe}_2\text{As}_2$ .

In this report our main attention falls on metals of multi-band type, with multiple FSs and many phase transitions at low temperatures. Fermi-surface instabilities at finite temperature form a topic of intense interest as of this writing [41]. Typical examples are  $\text{Sr}_2\text{Ru}_2\text{O}_7$  and many crystalline pnictides [42]–[44]. In such cases, finite-temperature effects ought to be considered within the relevant theories to be applied. Since serious finite-temperature DFT has not been attempted – in contrast with rather naive extrapolations of DFT at  $T = 0$  – many issues have now come to attention.

We first remark that  $k_F$  ceases to be a relevant parameter away from  $T = 0$ , for cases in which the condition  $\varepsilon_F \gg k_B T$  ceases to hold. Rather, when Fermi and thermal energies become comparable, a different wave-vector  $k_m$  comes into play, defined in terms of the actual chemical potential  $\mu(T)$  by

$$\frac{\hbar^2 k_m^2}{2m^*[\mu(T)]} + U(k_m) \equiv \mu(T)$$

where  $U$  is the momentum-dependent mean-field potential. For low temperature the sharpness of the FS still exists but only so long as  $k_B T \ll \mu$ .

There is already a remarkable example of a large finite-temperature effect that is inaccessible to simplistic extrapolations of zero-temperature methodology. Backes et al. [46] performed a

finite-temperature and -pressure DFT based on Born-Oppenheimer molecular dynamics for a Fe pnictide system. Their finite- $T$  results, in pronounced contrast with the electronic structure and FS computed at zero temperature, are new and entirely different [46]. The authors report that the band structure as well as the density of states, unlike those for  $T = 0$ , exhibit pronounced structural oscillations when measured at finite  $T$ . Oscillation of the band energies, particularly near the Fermi surface at ambient pressure, then leads to thermal broadening as expected.

The investigations by Backes et al. show that the FS at finite temperature has a conspicuously different behaviour in experimental observations, substantially at odds with DFT-based estimates relying on purely zero-temperature arguments. These need to be investigated further. Given these experimental findings, the finite-temperature aspects are undoubtedly missed by any effectively  $T = 0$  density functional calculation.

In contrast with the Backes et al. work, a recent instance of a conventional DFT calculation taken outside its proper limit of validity is provided by Sen et al. [45], who have advanced a misleading picture of the FS structure for FeAs-based pnictide materials at finite temperature. Their estimate is improperly generated in that what should be, inherently, a fully finite-temperature calculation is treated by an unjustified extension away from a strictly  $T = 0$  basis. We will expand this issue in a follow-up paper.

## 6. Conclusions

This brief overview deals with several nontrivial issues related to the ground-state predictions of density functional theory for metals. In particular we have reviewed what is needed for a clear and more faithful characterisations of the Fermi surface.

The FS is a central property of conducting electron systems, necessary for understanding their many physical properties. Transport and superconductivity are but two of them among a wide set of interesting and important many-body phenomena.

We started with a concise overview of the DFT, recognised as a first-principles theory for many-body systems. Since no real many-body problem can be solved exactly, the required systematic approximations to the many-body exchange-correlation functionals are outlined. Many computer codes, both general and specialised, rely on these approximations and are in widespread use in calculating almost every property, at least at zero temperature.

We have highlighted the Fermi surface as a special and especially delicate property of a Fermi system of carriers, and have looked at how one can use various experimental methods to map it: ARPES, SdH, dHvA, ARMRO and the interesting Kohn-anomaly technique. Since any measurements are carried out at finite temperature, we have emphasised the need for proper applications of finite-temperature theory rather than a too-casual stretching of strictly zero-temperature results. This becomes particularly evident when the Fermi energy of a metallic or semi-metallic material starts to enter the typical thermal scale. Uncritical extrapolations of  $T = 0$  results cannot but fall short of physical accuracy. At best (in the circumstances relevant to contemporary investigations) the claim of first-principles reliability cannot be supported in their case.

The importance of finite-temperature theory is argued in the context of some novel correlated electron systems, notably for those with phase changes at low temperatures. We believe there are some important aspects of the physics of “fermiology” that need serious extension, in not indeed a thoroughgoing re-evaluation.

Finally, we emphasise that for a number of crucial material properties, density functional theory has proved itself one of the most fruitful and rigorous tools for furthering progress in condensed-matter physics over the last half-century. Our aim here is far from criticising the theory or belittling its manifold deep successes. Density functional theory, as with all theoretical innovations, has limits. It is rather with a view to upholding the true strengths of DFT that we have visited some delicate, nonetheless themselves crucial, aspects of the response of materials

where the potential for uncritical misapplication of density functional arguments poses certain novel conceptual problems.

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## References

- [1] Engel E and Dreizler R M 2011 *Density Functional Theory* (Berlin: Springer)
- [2] Fiolhais C, Nogueira F and Marques M A L eds 2003 *A Primer in Density Functional Theory, Lect. Notes Phys.* **620** (Berlin: Springer)
- [3] Sholl D S and Steckel J A 2009 *Density Functional Theory: A Practical Introduction* (New York: John Wiley and Sons)
- [4] Capelle K 2006 *A Bird's-Eye View of Density-Functional Theory Brazilian J. Phys.* **36** 1318
- [5] Dobson J F, Vignale G and Das M P eds 1997 *Electronic Density Functional Theory: Recent Progress and New Directions* (New York: Plenum)
- [6] Burke K 2012 *Perspective on density functional theory J. Chem. Phys.* **136** 150901
- [7] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [8] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [9] Pines D and Nozières P 1966 *The Theory of Quantum Liquids Volume I: Normal Fermi Liquids* (New York: Benjamin)
- [10] Luttinger J M and Ward J C 1960 *Phys. Rev.* **118** 1417; Luttinger J M 1960 *Phys. Rev.* **119** 1158
- [11] Anisimov V and Izyumov Y 2010 *Electronic Structure of Strongly Correlated Materials* (Berlin: Springer) [Local density approximation and dynamical mean field theory compared]
- [12] Cabra D C, Honecker H and Pierre Pujol P eds 2012 *Modern Theories of Many-Particle Systems in Condensed Matter Physics* (Berlin: Springer) ch 4
- [13] Ylvisaker E R 2008 *DFT and DMFT: Implementations and Applications to the Study of Correlated Materials* (Davis: UC Thesis)
- [14] Rajagopal A K 1980 *Adv. Chem. Phys.* **41** 164
- [15] Martin R 2004 *Electronic Structure: Basic Theory and Practical Methods* (Cambridge: Cambridge University Press) p 137
- [16] Giuliani G and Vignale G 2005 *Quantum Theory of the Electron Liquids* (Cambridge: Cambridge University Press) sec 7.24
- [17] Kokko K and Das M P 1998 *J. Phys.: Condens. Matter* **10** 1285
- [18] Kurth S, Perdew J and Blaha P 1999 *Inter J. Quantum Chem.* **75** 889
- [19] Kordyuk A A 2014 *Low Temp. Phys.* **40** 286
- [20] Damaselli A, Shen Z-X and Hussain Z 2003 *Rev. Mod. Phys.* **75** 473
- [21] Hedin L 1965 *Phys. Rev.* **139** A790
- [22] Svane A, Christensen N E, Cardona M, Chantis A N, van Schilfgaarde M and Kotani Y 2010 *Phys Rev B* **81**
- [23] Aryasetiawan F 1992 *Phys RevB* **46** 13051
- [24] Georges A, Kotliar G, Krauth W and Rozenberg M 1996 *Rev. Mod. Phys.* **63** 13
- [25] Tomczak J M, Tomczak J M, van Schilfgaarde M and Kotliar G 2012 *Phys. Rev. Lett.* **109** 237010
- [26] Mearns D 1988 *Phys. Rev. B* **38** 5906
- [27] Schönhammer K and Gunnarsson O 1988 *Phys. Rev. B* **37** 3128 (1988)
- [28] Cohen M H and Wasserman A 2004 in *Proceedings of the International School of Physics "Enrico Fermi": The Physics of Complex Systems (New Advances and Perspectives)* Mallamace F and Stanley H E eds (Amsterdam: IOS Press) pp 253-295
- [29] Lamas C A Cabra D C and Grandi N 2008 *Phys. Rev. B* **78** 115104
- [30] Jiang H-M, Jiang Yao Z-J and Zhang F-C 2012 *Eur. Phys. J.* **100** 47004
- [31] Pourret A, Knebel G, Matsuda T D, Lapertot G and Flouquet J 2013 *J. Phys. Soc. Japan* **82** 053704
- [32] Edalati M, Lo K W and Phillips P W 2012 *Phys. Rev. D* **86** 086003
- [33] See reference [12] chapters 1 and 4.
- [34] Ziman J M *Theory of Solids* 1965 (Cambridge: Cambridge University Press)
- [35] Ohmichi E, Adachi H, Mori Y, Meano Y, Ishiguro T and Oguchi T 1999 *Phys. Rev. B* **59** 7263
- [36] Nam M S, Blundell S J, Ardavan A, Symington J A and Singleton J 2001 *J. Phys.: Condens. Matter* **13** 2271
- [37] Mermin N D 1965 *Phys. Rev. A* **137** 1441
- [38] Kohn W 1959 *Phys. Rev. Lett.* **2** 393
- [39] Soitsov M V and Petkov I Z 1988 *Annals of Physics* **184** 121

- [40] Backes S, Guterding D, Jeschke H O and Valenti R 2014 *New J. Phys.* **16** 083025
- [41] Rodriguez Ponte P, Cabra D C and Grandi N 2013 *Eur. Phys. J. B* **86** 85
- [42] Johnston D C 2010 *Adv. Phys.* **59** 83
- [43] Canfield P C and Bud'ko S L 2010 *Ann. Rev. Condens. Matter Phys.* **1** 27
- [44] Charnukha A *Charge Dynamics in 122 Iron Based Superconductors* 2014 (Berlin: Springer)
- [45] Sen S, Ghosh H, Sinha A K and Bharathi A 2014 *Supercond. Sci. Technol.* **27** 122003
- [46] Backes S and Jeschke H O 2013 *Phys Rev B* **88** 075111