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Inequivalence of the physical and Kohn-Sham Fermi surfaces

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The Fermi surface of an infinite system of interacting electrons is a sharply defined ground-state property. An exact solution of the Kohn-Sham equations of density-functional theory, which yields the correct physical density distribution and ground-state energy, also yields a Fermi surface. This paper shows by an example that, in general, the Kohn-Sham Fermi surface does not exactly reproduce the physical one.

I. INTRODUCTION

The Fermi surface (FS) of an extended system of interacting electrons is a well-defined ground-state property, described by wave vectors $\mathbf{k}$ for which the quasiparticle excitation energy $\tilde{\varepsilon}(\mathbf{k})$ equals the chemical potential.[1] In density-functional theory the Kohn-Sham[2] (KS) equations, which describe a *noninteracting* system with the same density $n(\mathbf{r})$ as the interacting one, also give rise to a Fermi surface. This raises the question: are the KS and physical FS's equivalent?[3,4] The main purpose of this paper is to demonstrate that the answer is, in general, no.

There are two trivial cases for which the FS's are equivalent: (1) in the absence of interactions, since the two systems are identical, and (2) for a uniform system, in which both FS's are spherical and enclose the same volume in $\mathbf{k}$ space.[1] Thus, any differences between the FS's must result from the combined effects of interactions, and inhomogeneities due to an external potential $v(\mathbf{r})$.[5]

In the following two sections we construct an example of a system which exhibits a Kohn-Sham FS that differs from the physical one. In Sec. II we consider the electron gas in a regime which permits a perturbative treatment of both the interactions and the external source. Section III is devoted to calculating the FS's in this regime. We conclude with some brief remarks in Sec. IV.

II. GENERAL FORMS OF THE FERMI SURFACES IN THE REGIME CONSIDERED

We consider an electron gas in a weak external potential,[6]

$$v(\mathbf{r})=\gamma\cos(\mathbf{q}\cdot\mathbf{r}) \tag{1}$$

$(\gamma \ll 1)$. It will be assumed that the density is high enough so that the interactions, as described by the Coulomb potential, $V(\mathbf{r})=e^2/r$, may also be regarded as weak $(e^2 \ll 1)$.[7]

The forms of the FS's to lowest order in γ and e^2 can be readily deduced by making the following observations, which apply to both FS's. First, the FS must be invariant under translations of $v(\mathbf{r})$ in space, i.e., under phase changes of the argument $\mathbf{q}\cdot\mathbf{r}$. In particular, for $\mathbf{q}\cdot\mathbf{r}\rightarrow\mathbf{q}\cdot\mathbf{r}+\pi$ we get $\gamma\rightarrow-\gamma$, so there can be no change in the FS to order γ. Also, the Fermi wave number (i.e., the magnitude of the Fermi wave vector) can depend only on the angle between $\mathbf{q}$ and the Fermi wave vector. Finally, there can be no shift in the FS of order e^2 alone ($\gamma=0$ term) because of the $\mathbf{k}$-space volume constraint.[1] Therefore, the KS and physical Fermi wave numbers can be written as

$$k_F(\nu)=1+\gamma^2k_F^{(2,0)}(\nu)+\gamma^2e^2k_F^{(2,1)}(\nu)\ , \tag{2}$$

$$\tilde{k}_F(\nu)=1+\gamma^2k_F^{(2,0)}(\nu)+\gamma^2e^2\tilde{k}_F^{(2,1)}(\nu)\ , \tag{3}$$

respectively, where

$$\nu=\mathbf{q}\cdot\mathbf{k}_F/qk_F=\mathbf{q}\cdot\tilde{\mathbf{k}}_F/q\tilde{k}_F\ , \tag{4}$$

and the wave numbers are measured in units of the unperturbed Fermi wave number. Since the two systems of particles are identical for $e^2=0$, $k_F^{(2,0)}(\nu)$ is common to both. The combined effects of interactions and external potential are represented by $k_F^{(2,1)}(\nu)$ and $\tilde{k}_F^{(2,1)}(\nu)$ which, as we shall see, are different.

Similarly, at the Fermi level[8] the excitation energies of the KS and physical systems, $\varepsilon(\mathbf{k})$ and $\tilde{\varepsilon}(\mathbf{k})$, respectively, have the forms

$$\varepsilon(\mathbf{k}_F)=\frac{k_F^2(\nu)}{2}+\gamma^2\Delta^{(2,0)}(\nu)+\gamma^2e^2\Delta^{(2,1)}(\nu)\ , \tag{5}$$

$$\tilde{\varepsilon}(\tilde{\mathbf{k}}_F)=\frac{\tilde{k}_F^2(\nu)}{2}+\gamma^2\Delta^{(2,0)}(\nu)+\gamma^2e^2\tilde{\Delta}^{(2,1)}(\nu)\ . \tag{6}$$

The first term in each of these equations corresponds to the free-electron contribution; the remaining terms will be calculated in the next section using ordinary perturbation theory.

We now substitute Eqs. (2) and (3) into Eqs. (5) and (6), apply the volume constraint[1]

$$\frac{1}{3\pi^2}=\frac{2}{(2\pi)^3}\int_{\mathcal{R}}d^3k \tag{7}$$

to each FS, where $\mathcal{R}$ is the region enclosed by the FS, and obtain

$$k_F^{(2,0)}(\nu)=-\Delta^{(2,0)}(\nu)+\int_0^1 d\nu'\Delta^{(2,0)}(\nu')\ , \tag{8}$$

$$k_F^{(2,1)}(\nu)=-\Delta^{(2,1)}(\nu)+\int_0^1 d\nu'\Delta^{(2,1)}(\nu') \ , \tag{9}$$

$$\tilde{k}_F^{(2,1)}(\nu)=-\tilde{\Delta}^{(2,1)}(\nu)+\int_0^1 d\nu'\tilde{\Delta}^{(2,1)}(\nu') \ . \tag{10}$$

III. CALCULATION OF THE FERMI SURFACES

To determine the functions $\Delta^{(2,0)}(\nu)$, $\Delta^{(2,1)}(\nu)$, and $\tilde{\Delta}^{(2,1)}(\nu)$, we will calculate to order $\gamma^2 e^2$ the shifts in $\varepsilon(\mathbf{k})$ and $\tilde{\varepsilon}(\mathbf{k})$ from the free-electron value $k^2/2$, and then evaluate them at $\mathbf{k}=\mathbf{k}_F$ and $\mathbf{k}=\tilde{\mathbf{k}}_F$, respectively. This evidently requires self-consistency since the unknowns being sought, $\mathbf{k}_F$ and $\tilde{\mathbf{k}}_F$, also serve as input.

The excitation energies $\tilde{\varepsilon}(\mathbf{k})$ are solutions of the Dyson equations,[9]

$$[-\tfrac{1}{2}\nabla^2+v(\mathbf{r})]\tilde{\psi}_{\mathbf{k}}(\mathbf{r})+\int d^3r'\Sigma(\mathbf{r},\mathbf{r}';\tilde{\varepsilon}(\mathbf{k}))\tilde{\psi}_{\mathbf{k}}(\mathbf{r}') =\tilde{\varepsilon}(\mathbf{k})\tilde{\psi}_{\mathbf{k}}(\mathbf{r}) \ , \tag{11}$$

where $\Sigma(\mathbf{r},\mathbf{r};\tilde{\varepsilon}(\mathbf{k}))$ is the proper self-energy. The KS equations,[2] which determine $\varepsilon(\mathbf{k})$, are

$$[-\tfrac{1}{2}\nabla^2+v_{\text{eff}}(\mathbf{r})]\psi_{\mathbf{k}}(\mathbf{r})=\varepsilon(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}) \ , \tag{12}$$

where

$$v_{\text{eff}}(\mathbf{r})=v(\mathbf{r})+\int d^3r' V(\mathbf{r}-\mathbf{r}')[n(\mathbf{r}')-n^{(0)}]+v_{\text{xc}}(\mathbf{r}) \tag{13}$$

is the effective local potential, $n^{(0)}=N/\Omega$,[10] where N is the number of electrons and Ω the volume of the system, and $v_{\text{xc}}(\mathbf{r})$ is the exchange-correlation potential. Solution of the Dyson equations to first order in e^2 is equivalent to a first order Hartree-Fock calculation.[7] Accordingly, we will be dealing with exchange only [$v_x(\mathbf{r})$ instead of $v_{\text{xc}}(\mathbf{r})$], and an eigenvalue-independent self-energy [$\Sigma(\mathbf{r},\mathbf{r}')$ instead of $\Sigma(\mathbf{r},\mathbf{r}';\tilde{\varepsilon}(\mathbf{k}))$].

In calculating the two FS's we shall find it convenient to separate the e^2 contributions into *direct* and *exchange* parts. The direct parts are equal and due to the second term of $v_{\text{eff}}(\mathbf{r})$ [Eq. (13)], which is common to $\Sigma(\mathbf{r},\mathbf{r}')$ and equal to its local part. It is the different treatments of exchange [local, in $v_x(\mathbf{r})$, and nonlocal, in $\Sigma(\mathbf{r},\mathbf{r}')$] which produce different FS's.

A. Kohn-Sham system

We now turn to the calculation of $k_F(\nu)$ [Eq. (2)], using the KS equations. The KS eigenvalues $\varepsilon(\mathbf{k})$ are determined by $v_{\text{eff}}(\mathbf{r})$, which requires calculation of $n(\mathbf{r})$. The unperturbed eigenfunctions are plane waves, and by orthogonality there is no shift in $\varepsilon(\mathbf{k})$ to first order in $v_{\text{eff}}(\mathbf{r})$.[11] Thus to compute $\varepsilon(\mathbf{k})$ to order γ^2, it is sufficient to determine $v_{\text{eff}}(\mathbf{r})$ to order γ.

The external potential $v(\mathbf{r})$ results in the density

$$n(\mathbf{r})=n^{(0)}+\gamma n(q)\cos(\mathbf{q}\cdot\mathbf{r}) \ , \tag{14}$$

where the linear response $n(q)$ is equal to the susceptibility, or static polarization propagator for the uniform electron gas, $\Pi(q,0)$,[7]

$$n(q)=\Pi_0(q,0)+e^2\Pi_1(q,0) \ . \tag{15}$$

By definition, the effective potential must induce the *same* linear response in the noninteracting (KS) system, for which the susceptibility is $\Pi_0(q,0)$. Thus, if we write

$$v_{\text{eff}}(\mathbf{r})=\gamma v_{\text{eff}}(q)\cos(\mathbf{q}\cdot\mathbf{r}) \ , \tag{16}$$

then from Eqs. (14) and (15),

$$n(\mathbf{r})=n^{(0)}+\gamma\Pi_0(q,0)v_{\text{eff}}(q)\cos(\mathbf{q}\cdot\mathbf{r}) \ . \tag{17}$$

Comparing Eqs. (14) and (17) we see, using Eq. (15), that

$$v_{\text{eff}}(q)=1+e^2\frac{\Pi_1(q,0)}{\Pi_0(q,0)} \ . \tag{18}$$

In order to determine the effects of exchange on the FS we need to isolate the exchange part of $v_{\text{eff}}(q)$. We can write the exchange potential as

$$v_x(\mathbf{r})=\gamma v_x(q)\cos(\mathbf{q}\cdot\mathbf{r}) \ . \tag{19}$$

Using Eqs. (14), (15), and (19) in Eq. (13) then yields

$$v_{\text{eff}}(q)=1+e^2\Pi_0(q,0)\bar{V}(\mathbf{q})+v_x(q) \ , \tag{20}$$

where

$$\bar{V}(\mathbf{q})=4\pi/q^2 \ . \tag{21}$$

Comparing Eqs. (18) and (20) we see that

$$v_x(q)=e^2\frac{\Pi_1^P(q,0)}{\Pi_0(q,0)} \ , \tag{22}$$

where

$$\Pi_1^P(q,0)=\Pi_1(q,0)-\bar{V}(\mathbf{q})[\Pi_0(q,0)]^2 \tag{23}$$

is the first order (in e^2) *proper* polarization propagator.[7]

With these results for $v_{\text{eff}}(\mathbf{r})$, we make a standard perturbation calculation to get the KS eigenvalues, and obtain

$$\varepsilon(\mathbf{k})=\frac{k^2}{2}+\gamma^2\varepsilon^{(2)}(\mathbf{k}) \ , \tag{24}$$

where

$$\varepsilon^{(2)}(\mathbf{k})=-\left[1+2e^2\left[\Pi_0(q,0)\bar{V}(\mathbf{q})+\frac{\Pi_1^P(q,0)}{\Pi_0(q,0)}\right]\right]\frac{q^2}{q^4-4(\mathbf{k}\cdot\mathbf{q})^2} \ . \tag{25}$$

To determine the Kohn-Sham FS we evaluate $\varepsilon(\mathbf{k})$ at $\mathbf{k}=\mathbf{k}_F$. From Eqs. (2), (4), (5), (24), and (25), we then find

$$\Delta^{(2,0)}(\nu)=-\frac{1}{q^2-4\nu^2} \tag{26}$$

and

$$\Delta^{(2,1)}(\nu)=\Delta_d^{(2,1)}(\nu)+\Delta_x^{(2,1)}(\nu) \ , \tag{27}$$

where

$$\Delta_d^{(2,1)}(\nu)=-2\Pi_0(q,0)\bar{V}(\mathbf{q})\frac{1}{q^2-4\nu^2} \ , \tag{28}$$

$$\Delta_x^{(2,1)}(\nu)=-2\frac{\Pi_1^P(q,0)}{\Pi_0(q,0)}\frac{1}{q^2-4\nu^2} \ , \tag{29}$$

are the direct and exchange contributions. It will be assumed that $q > 2$ so that no singularities appear in these quantities [by Eq. (4), ν is restricted to the range $-1 \leq \nu \leq 1$]. Finally, we use Eqs. (26)–(29) in Eqs. (8) and (9) to get

$$k_F^{(2,0)}(\nu) = \frac{1}{q^2-4\nu^2} - \frac{1}{4q} \ln \left[\frac{q+2}{q-2} \right] \tag{30}$$

and

$$k_F^{(2,1)}(\nu) = k_{F,d}^{(2,1)}(\nu) + k_{F,x}^{(2,1)}(\nu) \ , \tag{31}$$

where

$$\begin{aligned} k_{F,d}^{(2,1)}(\nu) &= -\Delta_d^{(2,1)}(\nu) + \int_0^1 d\nu' \Delta_d^{(2,1)}(\nu') \\ &= 2\Pi_0(q,0)\bar{V}(\mathbf{q}) \left[\frac{1}{q^2-4\nu^2} - \frac{1}{4q} \ln \left[\frac{q+2}{q-2} \right] \right] \ , \end{aligned} \tag{32}$$

$$\begin{aligned} k_{F,x}^{(2,1)}(\nu) &= -\Delta_x^{(2,1)}(\nu) + \int_0^1 d\nu' \Delta_x^{(2,1)}(\nu') \\ &= 2\,\frac{\Pi_1^p(q,0)}{\Pi_0(q,0)} \left[\frac{1}{q^2-4\nu^2} - \frac{1}{4q} \ln \left[\frac{q+2}{q-2} \right] \right] \ . \end{aligned} \tag{33}$$

Although $\Pi_0(q,0)$ can be evaluated analytically,[7] for general q, $\Pi_1^p(q,0)$ requires numerical computation.[12]

B. Physical system

To determine the physical FS we calculate $\tilde{k}_F^{(2,1)}(\nu)$ in Eq. (3), using the Dyson equations. To first order in e^2 the self-energy is[7]

$$\begin{aligned} \Sigma(\mathbf{r},\mathbf{r}') = {} & \delta(\mathbf{r}-\mathbf{r}') \int d^3r'' V(\mathbf{r}-\mathbf{r}')[n(\mathbf{r}'')-n^{(0)}] \\ & - V(\mathbf{r}-\mathbf{r}') \sum_{\mathbf{k}} \tilde{\psi}_{\mathbf{k}}(\mathbf{r}) \tilde{\psi}_{\mathbf{k}}^*(\mathbf{r}') \Theta(\mu - \tilde{\varepsilon}(\mathbf{k})), \end{aligned} \tag{34}$$

where $\Theta(x)$ is the step function

$$\Theta(x) = \begin{cases} 1, & x \geq 0 \\ 0, & x < 0 \end{cases} \tag{35}$$

and μ is the chemical potential. The two terms of $\Sigma(\mathbf{r},\mathbf{r}')$ are the direct and exchange parts, respectively. The direct part is local, and equivalent to the second term in $v_{\text{eff}}(\mathbf{r})$, Eq. (13). It therefore leads to the same direct terms in $\tilde{\varepsilon}(\mathbf{k})$ and $\tilde{k}_F(\nu)$ as found in $\varepsilon(\mathbf{k})$ and $k_F(\nu)$. Hence we can write

$$\tilde{\Delta}^{(2,1)}(\nu) = \Delta_d^{(2,1)}(\nu) + \tilde{\Delta}_x^{(2,1)}(\nu) \ , \tag{36}$$

$$\tilde{k}_F^{(2,1)}(\nu) = k_{F,d}^{(2,1)}(\nu) + \tilde{k}_{F,x}^{(2,1)}(\nu) \ , \tag{37}$$

where

$$\tilde{k}_{F,x}^{(2,1)}(\nu) = -\tilde{\Delta}_x^{(2,1)}(\nu) + \int_0^1 d\nu' \tilde{\Delta}_x^{(2,1)}(\nu') \ , \tag{38}$$

and focus attention on the exchange part of the Dyson eigenvalue $\tilde{\varepsilon}(\mathbf{k})$.

Let us make an expansion of $\tilde{\varepsilon}(\mathbf{k})$ in e^2,

$$\tilde{\varepsilon}(\mathbf{k}) = \tilde{\varepsilon}_0(\mathbf{k}) + e^2[\tilde{\varepsilon}_{1,d}(\mathbf{k}) + \tilde{\varepsilon}_{1,x}(\mathbf{k})] \ , \tag{39}$$

where

$$\tilde{\varepsilon}_0(\mathbf{k}) = \frac{k^2}{2} - \gamma^2 \frac{q^2}{q^4 - 4(\mathbf{k}\cdot\mathbf{q})^2} \tag{40}$$

and

$$\tilde{\varepsilon}_{1,d}(\mathbf{k}) = -2\gamma^2 \Pi_0(q,0) \bar{V}(\mathbf{q}) \frac{q^2}{q^4 - 4(\mathbf{k}\cdot\mathbf{q})^2} \tag{41}$$

are obtained with the results of the KS calculations (Sec. III A), and

$$\begin{aligned} \tilde{\varepsilon}_{1,x}(\mathbf{k}) = {} & -\sum_{\mathbf{k}'} \Theta(\mu - \tilde{\varepsilon}_0(\mathbf{k}')) \\ & \times \int d^3r\, d^3r' \bar{V}(\mathbf{r}-\mathbf{r}') \tilde{\psi}_{\mathbf{k}}^*(\mathbf{r}) \tilde{\psi}_{\mathbf{k}'}(\mathbf{r}) \\ & \times \tilde{\psi}_{\mathbf{k}'}^*(\mathbf{r}') \tilde{\psi}_{\mathbf{k}}(\mathbf{r}') \ . \end{aligned} \tag{42}$$

In writing Eq. (42) we have assumed that the eigenfunctions $\tilde{\psi}_{\mathbf{k}}(\mathbf{r})$ are normalized,

$$\int d^3r \, | \tilde{\psi}_{\mathbf{k}}(\mathbf{r}) |^2 = 1 \ . \tag{43}$$

To calculate $\tilde{\varepsilon}_{1,x}(\mathbf{k})$ we need the eigenfunctions to second order in γ, zeroth order in e^2. This involves a perturbation expansion in just $v(\mathbf{r})$, and the result is

$$\begin{aligned} \tilde{\psi}_{\mathbf{k}}(\mathbf{r}) = {} & \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\Omega^{1/2}} \left[1 - \tfrac{1}{2}\gamma^2 \left[\frac{1}{(q^2+2\mathbf{k}\cdot\mathbf{q})^2} + \frac{1}{(q^2-2\mathbf{k}\cdot\mathbf{q})^2} \right] \right] \\ & \times \left[1 - \gamma \left[\frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2+2\mathbf{k}\cdot\mathbf{q}} + \frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{q^2-2\mathbf{k}\cdot\mathbf{q}} \right] \right. \\ & \left. + O(\gamma^2) e^{\pm i2\mathbf{q}\cdot\mathbf{r}} \right] \ . \end{aligned} \tag{44}$$

The first factor involving γ^2 is due to the normalization, Eq. (43). In the second, the terms of order γ^2 do not contribute to the normalization, and integrate to $\delta_{\pm 2\mathbf{q},0} = 0$ in Eq. (42), so they need not be evaluated. Using Eq. (44) in Eq. (42) and integrating, we obtain

$$\begin{aligned} \tilde{\varepsilon}_{1,x}(\mathbf{k}) = {} & -\tfrac{1}{2}\Omega^{-1} \sum_{k'} \Theta(\mu - \tilde{\varepsilon}_0(\mathbf{k}')) \bar{V}(\mathbf{k}-\mathbf{k}') \\ & + \gamma^2 \Omega^{-1} \sum_{\mathbf{k}'}{}' [\Theta(1-k') - \Theta(1 - |\mathbf{k}'+\mathbf{q}|)] \bar{V}(\mathbf{k}-\mathbf{k}') \left[\frac{1}{q^2+2\mathbf{k}\cdot\mathbf{q}} - \frac{1}{q^2+2\mathbf{k}'\cdot\mathbf{q}} \right]^2 + (\mathbf{q} \to -\mathbf{q}) \ . \end{aligned} \tag{45}$$

We have used the even in $\mathbf{q}$ property of $\tilde{\varepsilon}_0(\mathbf{k})$ [Eq. (40)], hence the factor $\frac{1}{2}$ in the first term. The second term has a factor γ^2 so we have replaced $\Theta(\mu - \varepsilon_0(\mathbf{k}'))$ by $\Theta(1-k')$. By inspection of Eqs. (6), (36), and (39), we see that $\tilde{\Delta}_x^{(2,1)}(\nu)$ is equal to $\tilde{\varepsilon}_{1,x}(\tilde{\mathbf{k}}_F)$, up to an additive constant.[8] The sums in Eq. (45) may be converted to integrals and carried out almost completely; details are discussed in Appendix A. The result is

$$\tilde{\varepsilon}_{1,x}(\tilde{\mathbf{k}}_F)=\gamma^2\tilde{\Delta}_x^{(2,1)}(\nu)+C\ , \tag{46}$$

where C is a constant independent of ν, and

$$\begin{aligned}\tilde{\Delta}_x^{(2,1)}(\nu)=&\frac{1}{2\pi q^2}\left[\frac{\ln(q+\nu-1)}{q-2}-\frac{\ln(q+\nu+1)}{q+2}\right]-\frac{1}{2\pi(q^2-4\nu^2)}\left[1+\tfrac{1}{2}\ln\left[\frac{q^2-4\nu^2}{q^2-4}\right]-\frac{\nu}{q}\ln\left[\frac{q+2\nu}{q-2\nu}\right]\right]\\&+\frac{1}{2\pi q^2(q+2\nu)}\left\{(\tfrac{3}{2}+\ln 2)\ln\left[\frac{q+2}{q-2}\right]-\ln\left[\frac{q+\nu+1}{q+\nu-1}\right]\right.\\&\qquad-\ln(1+\nu)\ln\left[\frac{q+2\nu}{q-2}\right]-\ln(1-\nu)\ln\left[\frac{q+2}{q+2\nu}\right]+\frac{q}{(q^2+2\nu q+1)^{1/2}}\ln\left[\frac{(q^2+2\nu q+1)^{1/2}+1}{(q^2+2\nu q+1)^{1/2}-1}\right]\\&\qquad\left.+\int_{-1}^{1}\frac{dz}{q+2z}\left[2\ln|z-\nu|+4\ln(q+z+\nu)-\left[2+\frac{q+2\nu}{q+2z}\right]\ln|G(z)|\right]\right\}+(\nu\rightarrow-\nu)\ ,\end{aligned} \tag{47}$$

where

$$G(z)=2z(q+\nu)+q^2+2\nu q+2\nu^2+[4(q^2+2\nu q+1)z^2+4(q+\nu)(q^2+2\nu q+2)z+q^2(q+2\nu)^2+4(q+\nu)^2]^{1/2}\ . \tag{48}$$

Substitution of Eq. (47) in Eq. (38) yields $\tilde{k}_{F,x}^{(2,1)}(\nu)$.

C. Discussion

To summarize, we have shown that the Fermi wave numbers for the KS and physical systems may be written as

$$\begin{aligned}k_F(\nu)=&1+\gamma^2k_F^{(2,0)}(\nu)+\gamma^2e^2k_{F,d}^{(2,1)}(\nu)\\&+\gamma^2e^2k_{F,x}^{(2,1)}(\nu)\ ,\end{aligned} \tag{49}$$

$$\begin{aligned}\tilde{k}_F(\nu)=&1+\gamma^2k_F^{(2,0)}(\nu)+\gamma^2e^2k_{F,d}^{(2,1)}(\nu)\\&+\gamma^2e^2\tilde{k}_{F,x}^{(2,1)}(\nu)\ ,\end{aligned} \tag{50}$$

respectively. Equations (29) and (47) illustrate the difference in shapes of the FS's due to exchange, since $k_{F,x}^{(2,1)}(\nu)$ and $\tilde{k}_{F,x}^{(2,1)}(\nu)$ are equal to $-\Delta_x^{(2,1)}(\nu)$ and $-\tilde{\Delta}_x^{(2,1)}(\nu)$ up to additive constants. We observe a much more complex structure in $\tilde{k}_{F,x}^{(2,1)}(\nu)$ than in $k_{F,x}^{(2,1)}(\nu)$. These have not been evaluated for arbitrary $q>2$; however, exact results are available for the limit $q\rightarrow\infty$, which is discussed in Appendix B.

IV. CONCLUSIONS

We have shown here that the KS and physical FS's are in general different, by explicit construction of a representative example. We would like to comment on the practical consequences of this result.

The KS equations are used for approximate calculations of the band structure of solids and, in the case of metals, the FS.[3,4,13] One source of error is the necessarily approximate form of $v_{\mathrm{xc}}(\mathbf{r})$ used. What we have shown is that for an exact $v_{\mathrm{xc}}(\mathbf{r})$ the Kohn-Sham FS is generally not exact. Semiquantitative calculations are currently being carried out to estimate the magnitude of the discrepancy in real metals.

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APPENDIX A: EVALUATION OF $\tilde{\varepsilon}_{1,x}(\tilde{\mathbf{k}}_F)$

Here we discuss the calculation leading to Eq. (46). Taking the continuum limit $[\Omega^{-1}\sum_{\mathbf{k}}\rightarrow(2\pi)^{-3}\int d^3k]$ in Eq. (45) we find, after some manipulation,

$$\begin{aligned}\tilde{\varepsilon}_{1,x}(\tilde{\mathbf{k}}_F)=-I_0+\gamma^2\Bigg[&\frac{1}{q^2(q+2\nu)^2}(I_1-I_2)\\&-\frac{2}{q(q+2\nu)}(I_3+I_4)\\&+I_5-I_6\Bigg]+(\nu\rightarrow-\nu)\ ,\end{aligned} \tag{A1}$$

where

$$I_0=\frac{1}{4\pi^2}\int d^3p\frac{\Theta(\mu-\tilde{\varepsilon}_0(\mathbf{p}))}{(\mathbf{K}-\mathbf{p})^2}\ ,$$

$$\mathbf{K}=[1+\gamma^2k_F^{(2,0)}(\nu)]\mathbf{e}_\nu\ , \tag{A2}$$

$$I_1=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p})^2}\ , \tag{A3}$$

$$I_2=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p}+\mathbf{q})^2}\ , \tag{A4}$$

$$I_3=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p})^2}\frac{1}{q^2+2\mathbf{p}\cdot\mathbf{q}}\ , \tag{A5}$$

$$I_4=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p}+\mathbf{q})^2}\frac{1}{q^2-2\mathbf{p}\cdot\mathbf{q}}\ , \tag{A6}$$

$$I_5=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-p)^2}\frac{1}{(q^2+2\mathbf{p}\cdot\mathbf{q})^2}\ , \tag{A7}$$

$$I_6=\frac{1}{2\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p}+\mathbf{q})^2}\frac{1}{(q^2-2\mathbf{p}\cdot\mathbf{q})^2}\ , \tag{A8}$$

and $\mathbf{e}_\nu$ is a unit vector such that

$$\nu=\mathbf{e}_\nu\cdot\mathbf{q}/q\ . \tag{A9}$$

The integrals I_1–I_6 are straightforward to evaluate. The results are

$$I_1=\frac{1}{\pi}\ , \tag{A10}$$

$$I_2=\frac{1}{\pi}\left[1-\frac{q^2+2\nu q}{2(q^2+2\nu q+1)^{1/2}}\ln\left[\frac{(q^2+2\nu q+1)^{1/2}+1}{(q^2+2\nu q+1)^{1/2}-1}\right]\right]\ , \tag{A11}$$

$$I_3=\frac{1}{4\pi q}\left[\ln(1+\nu)\ln\left[\frac{q+2\nu}{q-2}\right]+\ln(1-\nu)\ln\left[\frac{q+2}{q+2\nu}\right]\right]-\frac{1}{2\pi q}\int_{-1}^{1}dz\frac{\ln|z-\nu|}{q+2z}\ , \tag{A12}$$

$$I_4=-\frac{\ln 2}{4\pi q}\ln\left[\frac{q+2}{q-2}\right]-\frac{1}{2\pi q}\int_{-1}^{1}\frac{dz}{q+2z}[2\ln(q+z+\nu)-\ln|G(z)|]\ , \tag{A13}$$

$$I_5=\frac{1}{4\pi q^2(q+2\nu)}\ln\left[\frac{q+2}{q-2}\right]\ , \tag{A14}$$

$$I_6=-\frac{1}{2\pi q^2}\left[\frac{2\ln 2}{q^2-4}+\frac{\ln(q+\nu-1)}{q-2}-\frac{\ln(q+\nu+1)}{q+2}\right.$$
$$\left.+\frac{1}{q+2\nu}\ln\left[\frac{(q+2)(q+\nu-1)}{(q-2)(q+\nu+1)}\right]-\int_{-1}^{1}\frac{dz}{(q+2z)^2}\ln|G(z)|\right]\ , \tag{A15}$$

where

$$G(z)=2z(q+\nu)+q^2+2\nu q+2\nu^2+[4(q^2+2\nu q+1)z^2+4(q+\nu)(q^2+2\nu q+2)z+q^2(q+2\nu)^2+4(q+\nu)^2]^{1/2}\ . \tag{A16}$$

We are left with evaluating I_0.

Evaluation of I_0. In Eq. (A2), we need the chemical potential to second order in γ. In zeroth order it is equal to $\frac{1}{2}$, corresponding to the free-electron system. Let us write

$$\mu=\tfrac{1}{2}+\gamma^2\mu^{(2)} \tag{A17}$$

and

$$\tilde{\varepsilon}_0(\mathbf{p})=\frac{p^2}{2}+\gamma^2\tilde{\varepsilon}_0^{(2)}(\mathbf{p})\ , \tag{A18}$$

where

$$\tilde{\varepsilon}_0^{(2)}(\mathbf{p})=-\frac{q^2}{q^4-4(\mathbf{p}\cdot\mathbf{q})^2} \tag{A19}$$

[see Eq. (40)]. Then with

$$\mu=\tilde{\varepsilon}_0\{[1+\gamma^2k_F^{(2,0)}(\nu)]\mathbf{e}_\nu\}\ , \tag{A20}$$

we obtain

$$\mu^{(2)}=k_F^{(2,0)}(\nu)+\tilde{\varepsilon}_0^{(2)}(\mathbf{e}_\nu)\ . \tag{A21}$$

Before using these expressions in I_0, we make the change of variable $\mathbf{p}\to\mathbf{p}+\gamma^2k_F^{(2,0)}(\nu)\mathbf{e}_\nu$ to get

$$I_0=\frac{1}{4\pi^2}\int\frac{d^3p}{(\mathbf{e}_\nu-\mathbf{p})^2}\Theta[\mu-\tilde{\varepsilon}_0(\mathbf{p}+\gamma^2k_F^{(2,0)}(\nu)\mathbf{e}_\nu)]\ . \tag{A22}$$

All the γ dependence is now contained in the step function, which has the expansion

$$\Theta(\mu-\tilde{\varepsilon}_0(\mathbf{p}+\gamma^2k_F^{(2,0)}(\nu)\mathbf{e}_\nu))$$
$$=\Theta(1-p)+\gamma^2k_F^{(2,0)}(\nu)\delta(1-p)(1-\mathbf{e}_\nu\cdot\hat{\mathbf{p}})$$
$$-\gamma^2\delta(1-p)[\tilde{\varepsilon}_0^{(2)}(\hat{\mathbf{p}})-\tilde{\varepsilon}_0^{(2)}(\mathbf{e}_\nu)]\ , \tag{A23}$$

where $\hat{\mathbf{p}}=\mathbf{p}/p$. Substituting in Eq. (A22), we obtain

$$I_0=I_0^{(0)}+\gamma^2(I_{0,a}^{(2)}+I_{0,b}^{(2)})\ , \tag{A24}$$

where

$$I_0^{(0)}=\frac{1}{4\pi^2}\int d^3p\frac{\Theta(1-p)}{(\mathbf{e}_\nu-\mathbf{p})^2}=\frac{1}{2\pi}\ , \tag{A25}$$

$$I_{0,a}^{(2)}=\frac{1}{4\pi^2}k_F^{(2,0)}(\nu)\int d^3p\,\delta(1-p)\frac{1-\mathbf{e}_\nu\cdot\hat{\mathbf{p}}}{(\mathbf{e}_\nu-\hat{\mathbf{p}})^2}$$

$$=\frac{1}{2\pi}k_F^{(2,0)}(\nu)$$

$$=\frac{1}{2\pi}\left[\frac{1}{q^2-4\nu^2}-\frac{1}{4q}\ln\left|\frac{q+2}{q-2}\right|\right], \tag{A26}$$

$$I_{0,b}^{(2)}=\frac{1}{4\pi^2}\int_{-1}^{1}d^3p\frac{\delta(1-p)}{(\mathbf{e}_\nu-\hat{\mathbf{p}})^2}[\tilde{\varepsilon}_0^{(2)}(\mathbf{e}_\nu)-\tilde{\varepsilon}_0^{(2)}(\hat{\mathbf{p}})]\ . \tag{A27}$$

Using Eq. (A19) and performing the integrations, we find

$$I_{0,b}^{(2)}=\frac{1}{4\pi q(q^2-4\nu^2)}\left[q\ln\left|\frac{q^2-4\nu^2}{q^2-4}\right|\right.$$
$$\left.-2\nu\ln\left|\frac{q+2\nu}{q-2\nu}\right|\right]. \tag{A28}$$

Finally, substituting Eqs. (A25), (A26), and (A28) in Eq. (A24), we get the result

$$I_0=\frac{1}{2\pi}-\gamma^2\frac{1}{8\pi q}\ln\left|\frac{q+2}{q-2}\right|$$
$$+\gamma^2\frac{1}{2\pi(q^2-4\nu^2)}$$
$$\times\left[1+\tfrac{1}{2}\ln\left|\frac{q^2-4\nu^2}{q^2-4}\right|-\frac{\nu}{q}\ln\left|\frac{q+2\nu}{q-2\nu}\right|\right]. \tag{A29}$$

Substituting Eqs. (A10)–(A15) and (A29) in Eq. (A1) yields Eq. (46).

APPENDIX B: FERMI SURFACES IN THE LIMIT $q\rightarrow\infty$

It is of interest to consider the asymptotic forms of the FS's in the limit $q\rightarrow\infty$, since exact results are available.

For large q, the first-order proper polarization propagator of Sec. III A has the form[14] $\Pi_1^p(q,0)=O(q^{-6})$. (The numerical factor is unimportant for our purposes.) Since[7] $\Pi_0(q,0)=O(q^{-2})$, Eq. (29) becomes

$$\Delta_x^{(2,1)}(\nu)=O(q^{-6})(1+4\nu^2q^{-2}+\cdots) \tag{B1}$$

so that, from Eq. (33),

$$k_{F,x}^{(2,1)}(\nu)=O(q^{-8})(\nu^2-\tfrac{1}{3})\ . \tag{B2}$$

On the other hand, Eq. (47) has the asymptotic form

$$\tilde{\Delta}_x^{(2,1)}(\nu)=O(q^{-2})[1+2(1-\nu^2)q^{-2}+\cdots]\ , \tag{B3}$$

which, by Eq. (38), leads to

$$\tilde{k}_{F,x}^{(2,1)}(\nu)=O(q^{-4})(\nu^2-\tfrac{1}{3})\ . \tag{B4}$$

Equations (B2) and (B4) show that the distortions of the FS's due to exchange differ by 4 orders of magnitude in q^{-1}. This might seem peculiar. After all, by definition the *densities* of the two systems must have the same asymptotic form. Why should their FS's be so different? Briefly, this can be explained as follows.

It is easy to show that the exchange part of $\varepsilon(\mathbf{k})$ can be written as

$$\varepsilon_x(\mathbf{k})=\langle\psi_{\mathbf{k}}^x\,|\,v\,|\,\mathbf{k}\rangle+\text{c.c.}\ , \tag{B5}$$

where $\psi_{\mathbf{k}}^x(\mathbf{r})$ is the exchange term of $\psi_{\mathbf{k}}(\mathbf{r})$ [i.e., the shift in $\psi_{\mathbf{k}}(\mathbf{r})$ involving $v_x(\mathbf{r})$], and $|\,\mathbf{k}\rangle$ is a plane-wave state. The shift $\psi_{\mathbf{k}}^x(\mathbf{r})$ has the same asymptotic behavior as the exchange part of the density, which is proportional to $\Pi_1^p(q,0)$ and hence behaves like q^{-6}. This results in a contribution of order q^{-6} in $\varepsilon_x(\mathbf{k})$ which is uniform (independent of $\mathbf{k}$), and hence does not affect the FS. The distortion of the FS shows up in the next higher order, which is q^{-8}, hence Eq. (B2).

By contrast, the exchange part of $\tilde{\varepsilon}(\mathbf{k})$ is

$$\tilde{\varepsilon}_x(\mathbf{k})=\langle\mathbf{k}\,|\,\Sigma\,|\,\mathbf{k}\rangle+(\langle\tilde{\psi}_{\mathbf{k}}^x\,|\,v\,|\,\mathbf{k}\rangle+\text{c.c.})\ , \tag{B6}$$

where $\tilde{\psi}_{\mathbf{k}}^x(\mathbf{r})$ is the exchange term of $\tilde{\psi}_{\mathbf{k}}(\mathbf{r})$ [i.e., the shift in $\tilde{\psi}_{\mathbf{k}}(\mathbf{r})$ involving the second term in Eq. (34)]. Were it not for the first term in Eq. (B6), the same arguments as in the preceding paragraph would lead to a $\tilde{k}_{F,x}^{(2,1)}(\nu)$ of order q^{-8}. But $\langle\mathbf{k}\,|\,\Sigma\,|\,\mathbf{k}\rangle$ behaves like q^{-4}, and induces a nonuniform shift to the same order in $\tilde{\varepsilon}_x(\mathbf{k})$, hence Eq. (B4).

The orders of magnitude in q^{-1} discrepancy between the KS and physical FS's is a patently nonlocal effect. The $\mathbf{k}$-dependent term $\langle\mathbf{k}\,|\,\Sigma\,|\,\mathbf{k}\rangle$ appearing in Eq. (B6) can have no counterpart in Eq. (B5) from the effective local potential, since $\langle\mathbf{k}\,|\,v_{\text{eff}}\,|\,\mathbf{k}\rangle=0$.[11]

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