Exact Calculation of the Orthogonality Catastrophe in Metals

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We give exact calculation, using the linked-cluster theorem, of the overlap between the ground-state wave functions of a system of N fermions in the absence and in the presence of a localized potential. It is found that the overlap vanishes as $N^{-\alpha}$, where $\alpha(\delta)$ contains both a nonperiodic and a π-periodic term in the phase shift $\delta(\epsilon_F)$ due to the potential. The present result reduces to that of Anderson and of Nozières and de Dominicis for small phase shifts.

It has been shown by Anderson[1] that the ground states of a system of many fermions in the absence and in the presence of a localized potential are orthogonal to each other. This "orthogonality catastrophe" is indirectly observable in the response of a Fermi gas to the sudden application of a potential, as in the edge of the x-ray absorption and emission spectra in metals.[2] The orthogonality causes the quenching of the zero-excitation line, while the edge singularity is related to the corresponding high density of low-energy pair excitations.[3]

We present in this Letter an exact and direct calculation of the overlap between ground states with and without the potential. The motivations for an exact calculation are several: First, to investigate the domain of validity of former calculations.[2,4] It can be asked[5] whether the overlap should be a π-periodic function of the phase shift as are all the stationary properties of metals and alloys which can be described in terms of scattering of conduction electrons,[6] except, curiously, the Friedel sum rule. A periodicity implies that the sudden application of a potential sufficient to extract or destroy an electronic state (resonant or bound), $\delta_F = \pi$, would be equivalent in its effect on the Fermi sea to no potential at all. This does not seem very likely, and the present analysis will allow us to distinguish between purely transient and secondary screening effects. Moreover, the present calculation is carried out in a way which is directly applicable to the x-ray problem.

Consider the problem of x-ray emission. A deep hole is suddenly filled by an electron of the Fermi sea. The potential seen by the latter is therefore switched off at time $t=0$, as[7]

$$\hat{V}^e = \lim_{\eta\to 0} V\theta(-t)\exp\eta t\sum_{kk'} a_k^\dagger a_{k'}. \tag{1}$$

At $t=-\infty$, the ground state of the system is that of a Fermi sea in absence of potential, $|0\rangle$. The potential is switched on adiabatically. At time t the system has evolved in the presence of the potential, to a state written in the interaction representation as ($\hbar=1$)

$$|\Psi(t)\rangle = \hat{S}(t,-\infty)|0\rangle = T\{\exp[-i\textstyle\int_{-\infty}^{t} dt'\,\hat{V}_I^e(t')]\}|0\rangle, \tag{2}$$

where $S(t)$ is the evolution operator or S matrix. The state $|\Psi(t)\rangle$ corresponds to the ground state of the system for $t<0$.[8] At $t=0$, the potential (1) is suddenly switched off. While the state of the system remains unchanged[9] [$|\Psi(t)\rangle$ is time independent for $t>0$], it no longer corresponds to the ground state of the system, which is now $|0\rangle$. The quantity of interest is the overlap between $|\Psi(t)\rangle$ and the ground state of the system at some time $t>0$, which is equal to the overlap between ground states just before ($t=0^-$) and after ($t=0^+$) the switchoff. This overlap may be written as

$$\langle 0|1\rangle_e = \langle 0|\hat{S}(t,-\infty)|0\rangle = \langle 0|\hat{S}(\infty,-\infty)|0\rangle \tag{3}$$

which is the ground-state expectation value of the S matrix.[10] The zero-excitation line intensity is given directly by the square of the modulus of the overlap

$$|\langle\Psi(t>0)|0\rangle|^2 = |\langle 1|0\rangle|^2. \tag{4}$$

Similarly, the x-ray absorption can be seen as a time-reversed emission problem. The overlap is given in this case by

$$\langle 1|0\rangle_a = \langle 0|S(\infty,t)|0\rangle^* = \langle 0|S(\infty,-\infty)|0\rangle^* \tag{5}$$

for some $t<0$, with a potential $\hat{V}^a(t) = \hat{V}^e(-t)$.

To evaluate the overlap, one makes use of the linked-cluster theorem[11] and obtains (the upper/lower sign corresponding to the emission/absorption case)

$$\ln\langle\hat{S}\rangle=\langle\hat{S}\rangle_c-1=-\sum_{n=1}^{\infty}V^n n^{-1}\int dt_1\,\theta(\mp t_1)\cdots\int dt_n\,\theta(\mp t_n)g(t_1-t_2)\cdots g(t_n-t_1)=-\int_0^1 d\lambda\,V\int dt\,\theta(\mp t)\varphi(t,t), \tag{6}$$

where $g=\sum g_k$ is the free Fermi-gas propagator. The factor n^{-1} or the integral over the fictitious coupling constant λ is needed to avoid overcounting. The function $\varphi(t,t)$ is the $t=t'$ limit of the double-time Green's function $\varphi(t,t')=\sum_{kk'}\varphi_{kk'}(t,t')$, which obeys the differential equation

$$(i\partial_t-\epsilon_k)\varphi_{kk'}(t,t')-\lambda V\theta(\mp t)\textstyle\sum_q\varphi_{qk'}(t,t')=\delta_{kk'}\delta(t-t'). \tag{7}$$

After performing a Fourier transform over the variable t, Eq. (7) becomes a singular integral equation

$$\varphi(\omega,t')\pm g^{\pm}(\omega)\lambda V(2i\pi)^{-1}\int d\omega'(\omega'-\omega-i\eta)^{-1}\varphi(\omega',t')=g^{\pm}(\omega)e^{i\omega t'} \tag{8}$$

with a simple Cauchy kernel. The quantities $g^-=g$ and $g^+=g/(1-\lambda Vg)$ are the absorption and emission Green's function of Nozières and de Dominicis (ND).[2]

The solution of integral equations of the type (8) is obtained by reduction to a Hilbert boundary problem.[12] One derives the following exact expression for the Green's function:

$$\varphi(\omega,t')=g^{\pm}e^{i\omega t'}\mp g^{\pm}e^{\pm L}\lambda V(2i\pi)^{-1}\int d\omega'(\omega'-\omega-i\eta)^{-1}e^{i\omega' t'}g^{\mp}e^{\mp L}, \tag{9}$$

where $L=(2i\pi)^{-1}\int d\omega'(\omega'-\omega-i\eta)^{-1}\ln(1-\lambda Vg)$ is a complex phase factor due to the transient nature of the potential.[13] The symmetry between the emission and the absorption problems is evident. The Green's function (9) reduces to the result of ND in the asymptotic limit $|t-t'|\to\infty$.[14] Performing the remaining integral in (6), one obtains

$$\int dt\,\theta(\mp t)\varphi(t,t)=\int dt\,\theta(\mp t)g^-(t=0^-)+\lambda V(2\pi)^{-2}\int d\omega\int d\omega'[(\omega'-\omega)^2+\eta^2]^{-1}[g^+e^L](\omega)[g^-e^{-L}](\omega'). \tag{10}$$

The singular first term of Eq. (10) is purely imaginary and does not contribute to the zero-excitation line intensity. The second term is identical for the emission and absorption cases: They have the same overlap, as expected from time-reversal symmetry [Eqs. (4) and (5)]. The overlap is evaluated by contour integration, using the spectral representation of the Green's function,[15] to yield the exact result

$$\mathrm{Re}\ln\langle\hat{S}\rangle=\int_0^1 d\lambda\,\lambda V^2\int_{\mu}^{\infty}d\omega_1\int_{-\infty}^{\mu}d\omega_2\,\tfrac{3}{2}[B^+(\omega_1)A^-(\omega_2)+B^-(\omega_1)A^+(\omega_2)](\omega_2-\omega_1)^{-2}. \tag{11}$$

The argument is singular at the Fermi level (infrared catastrophe). The stationary spectral densities $A^{\pm}=-\pi^{-1}\mathrm{Im}g^{\pm}$, $B^{\pm}=\pi^{-1}\mathrm{Im}g^{\pm}$, occur alone in the integral of (11), the phase factors canceling out. This means that in its effect, the transient character of the potential occurs at two times only. Assuming the spectral densities to be smooth functions of the energy, they can be taken out of the integral. The singular part of the latter is readily evaluated:

$$\int_{\mu}^{w}d\omega'\int_0^{\mu}d\omega''(\omega'-\omega'')^{-2}\simeq-\ln(\Delta/\mu)\simeq\tfrac{1}{3}\ln N, \tag{12}$$

where $\Delta=CN^{-1/3}$ is the difference between electronic energy levels in a box of volume ρN (N is the number of ions or the number of electrons in the Fermi sea). The quantity $C=\pi^{5/3}6^{1/3}\hbar^2m^{-1}\rho^{2/3}$ is of order of the Fermi energy μ, and the bandwidth w is introduced as an upper cutoff in Eq. (12). Combining Eqs. (3), (11), and (12), one recovers Anderson's orthogonality theorem,[1] namely

$$|\langle 0|1\rangle|=N^{-\alpha}, \tag{13}$$

where

$$\alpha=-\int_0^1 d\lambda\,\lambda V^2\tfrac{1}{2}[B^+(\mu)A^-(\mu)+B(\mu)A^+(\mu)]. \tag{14}$$

Introducing the following notations for the Green's function of the free Fermi gas, $G^0(\omega)=I(\omega)-i\pi n(\omega)$, $\tan\theta=I(\omega_F)/\pi n(\omega_F)$, and recalling the well-known expression for the phase shift in the presence of a stationary localized potential λV,[16] $\tan\delta=-\pi n\lambda V/(1-I\lambda V)$, one obtains for α the relation

$$\alpha=\pi^{-2}\int d\lambda\,\lambda^{-1}\sin^2\delta_F=-\pi^2\cos^2\theta[\delta_F\tan\theta+\ln|\cos\delta_F-\tan\theta\sin\delta_F|] \tag{15}$$

which is plotted in Fig. 1. Equation (15) represents a new, exact relation for the overlap. The principal feature of our result is that $\alpha(\delta_F)$ splits into a term linear in the phase shift at the Fermi surface δ_F, $\alpha_1 = (-\frac{1}{2})\pi^{-2}\sin 2\theta\delta_F$, and a π-periodic contribution, $\alpha_2 = -\pi^{-2}\cos^2\theta[\ln|\cos(\theta+\delta)| - \ln|\cos\theta|]$. Although our particular choice of the potential (1) restricts the phase shift to the interval $[-\pi/2-\theta, \pi/2-\theta]$, it can be noticed that the minimum of orthogonality corresponds to phase shifts which are multiple of π, i.e., for perfect screening of the deep hole. The nonperiodic behavior arises from the overcounting integration only [cf. Eq. (15)]. For the Green's function, on the other hand, it appears in the phase factors $\exp L$ in Eq. (8). These phase factors, essential in the asymptotic limit $|t-t'|\to\infty$,[2] cancel in the opposite limit $|t-t'|=0$ which enters the calculation of α. The asymptotic limit of ND is therefore inadequate to calculate overlap, except for small phase shifts.

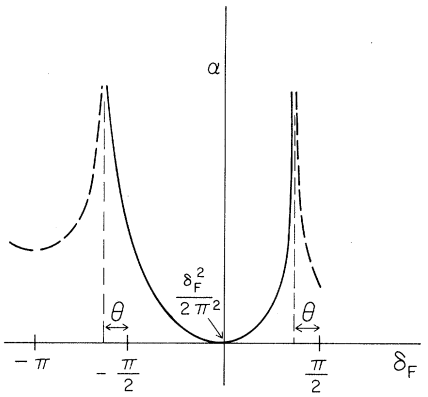

FIG. 1. The overlap exponent α as a function of the phase shift. α can be written as the sum of a linear and a π-periodic contribution. One recovers Anderson's result for small phase shifts.

The orthogonality disappears identically for $\theta=\pi/2$, i.e., for an insulator or a semiconductor (where $\delta_F=\pi$ though $n_F=0$). The zero-excitation line remains finite, as is well known in these solids.

For small phase shifts, one recovers the result of ND and Anderson,[2,4] $\alpha \simeq \delta_F^2/2\pi^2$, which is indeed the first term of an expansion in powers of δ_F, as was hinted by Friedel.[5,17] In a perturbative approach in powers of the potential V, the first contribution to the modulus of the overlap is of second order. From Eq. (6), one obtains $\alpha = \frac{1}{2}N_F V^2$, which is the result of Schotte and Schotte.[18] For an infinite potential, i.e., $\delta_F = (n+\frac{1}{2})\pi-\theta$, the orthogonality is maximal ($\alpha=\infty$) and independent of the size of the sample, as was to be expected. Our result can be seen as an interpolation between the small phase-shift value of Anderson and ND, and the physical requirement of maximum orthogonality for $|V|=\infty$.

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[1]P. W. Anderson, Phys. Rev. Lett. 18, 1049 (1967).

[2]P. Nozières and C. T. de Dominicis, Phys. Rev. 178, 1097 (1969).

[3]J. J. Hopfield, Comments Solid State Phys. 2, 40 (1969).

[4]P. W. Anderson, Phys. Rev. 164, 352 (1967).

[5]J. Friedel, Comments Solid State Phys. 2, 21 (1969).

[6]The statement is implicit in V. Heine, in *Physics of Metals*, edited by J. Ziman (Cambridge Univ., Cambridge, England, 1969), pp. 5 and 26. We should like to thank Dr. D. L. Weaire for pointing this out to us.

[7]This form of a potential corresponds to a delta function potential or, in a tight-binding nondegenerate band, to a potential localized at the deep hole site. A separable potential gives formally the same results (cf. Ref. 2, Sec. III). These are the only cases where the momentum sum can be performed, and the stationary problem solved in a closed form. Qualitatively this restriction should not affect the present result for the transient problem.

[8]The ground state obtained by adiabatically switching on the potential is identical to the true emission ground state since the metal has a finite (though large) volume: The difference Δ between electronic energy levels is finite, hence an η can be found such that $\eta \ll \Delta \propto N^{-1/3}$, which is the criterion of applicability of the adiabatic principle [A. B. Migdal, *Approximation Methods in Quantum Mechanics* (Benjamin, New York, 1969), p. 83, or E. Müller-Hartmann, T. V. Ramakrishman, and G. Toulouse, Phys. Rev. B (to be published)].

[9]The Auger effect and the electron-electron interaction in the Fermi sea have been neglected, as in the classical work on the subject (Refs. 2 and 3). For a discussion of the effect of a finite lifetime of the deep hole, see Müller-Hartmann, Ramakrishnan, and Toulouse, Ref. 8, or B. Roulet, J. Gavoret, and P. Nozières, Phys. Rev. 178, 1072 (1969).

[10]In some problems like the nuclear β decay, the transition probability is directly related to the overlap

$$W = |\langle 1|0\rangle|^2 = |\langle 0|\hat{S}|0\rangle|^2$$

(cf. Migdal, Ref. 8, p. 73). This is not the case in the x-ray problem as initial and final ground states have different numbers of electrons in the Fermi sea. There is still a simple relation between overlap and transition probability, however [cf. Ref. 2, Eq. (15), or Ref. 3, p. 48].

[11]A. A. Abrikosov, L. P. Gor'kov, and I. Ye. Dzyaloshinskii, *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, New York, 1965), p. 130.

[12]N. I. Muskhelishvili, in *Singular Integral Equations*, edited by J. Radok (Noordhoff, Groningen, The Netherlands, 1958), pp. 123-127. The arbitrary constant is taken to be zero since $\varphi \to 0$, hence $\int d\omega' (\omega' - \omega - i\eta)^{-1} \varphi(\omega') \to 0$ as $|\omega| \to \infty$. The index is zero. The generalization of the Hilbert problem to distributions (like g or φ) is due to H. A. Lauwerier, Arch. Ration. Mech. Anal. 13, 157 (1967).

[13]L is directly related to the phase shift $\delta(\omega)$: $L = -\pi^{-1} \int d\omega' (\omega' - \omega - i\eta) \theta(\omega') \delta(\omega')$, as obtained by expressing the Green's function g in terms of its advanced counterpart (Ref. 11, p. 56).

[14]With the asymptotic form of $g^{\mp}$ suggested by ND, Eq. (9) yields asymptotically in t and t' the result of Ref. 2 for $\varphi(t,t')$ [i.e., their Eq. (51) with $t = \infty$, $t' = 0$ and their Eq. (53) with $t = -\infty$, $t' = 0$], as can be verified by Lighthill's technique [M. J. Lighthill, *Fourier Analysis and Generalised Functions* (Cambridge Univ., Cambridge, England, 1958), Chap. 4]. The comparison cannot be pushed further since (i) ND's $g^{\mp}$ do not satisfy Lehmann's spectral representation, and (ii) the asymptotic limit is not suitable for the evaluation of the overlap.

[15]Ref. 11, p. 55.

[16]J. Friedel, in *Theory of Magnetism in Transition Metals, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII,* edited by W. Marshall (Academic, New York, 1967), p. 296.

[17]To obtain the overlap coefficient α, Anderson uses an expansion in powers of δ_F [Ref. 4, Eqs. (12) and (13)] and integrates over each term of the expansion separately. A series may be integrated term by term only within its domain of convergence (i.e., for small δ_F). Anderson's result is therefore valid only for small δ_F. The asymptotic solution of ND for the overlap corresponds to a small phase shift approximation since their Eq. (55) is in fact equivalent to an expansion in powers of δ_F.

[18]K. D. Schotte and U. Schotte, Phys. Rev. 182, 479 (1969). This is not entirely unexpected in view of these authors' picture of the Fermi sea as a set of harmonic oscillators [cf. their Eqs. (17) and (18)]. The potential acts to shift these oscillators. The linked-cluster expansion of the evolution operator [their Eq. (22)] gives only a second-order contribution: All higher terms vanish. The related problem of the line shape of an oscillating system subject to a Gaussian random-frequency modulation exhibits a similar disappearance of the higher order terms in the cumulant expansion of the characteristic function of the power spectrum [cf. R. Kubo, in *Fluctuations, Relaxation, and Resonance in Magnetic Systems,* edited by D. ter Haar (Oliver and Boyd, London, England, 1962), p. 23].

Anomalous Metal-Semiconductor Tunneling Near the Mott Transition*

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Anomalous features observed in the tunneling spectra of Schottky barrier junctions on Si:B are related to Hubbard's model of the metallic (Mott) transition.

We have observed an anomalous zero-bias resistance peak in metal-semiconductor (Schottky barrier) tunnel junctions which appears as the semiconductor impurity concentration approaches the Mott critical value N_c.[1] Evidence suggests that this peak is the result of a gap, or sharp minimum, at the Fermi energy, in the density of final states in the semiconductor. Broadening of these states, consistent with Hubbard's model,[2] is observed with a superconducting counterelectrode as a concentration-dependent broadening of the BCS density-of-states peaks. The resistance peak is increased by large magnetic fields. Similarity between this behavior and anomalous positive magnetoresistance in the semiconductor substrate supports our interpretation if, at N_c, the tunneling final states occur near the reserve region[3] in the electrode. In addition, we show that the real-intermediate-state tunneling model of Giaever and Zeller[4,5] is highly instructive as an approximate interpretation of the experimental results.

In spite of continuing interest in the Mott transition,[1] predictions based on the Hubbard Hamil-