zinc[6-8] show no change in ΔH (to within the experimental uncertainty of ±0.2 kcal/mole), it would appear that the combination of relaxation displacements that places $(\partial\Delta S/\partial p)_T$ towards the low end of the calculated range is most probable. On the other hand, the parameters in Eq. (8) can be varied over reasonable limits to yield changes in ΔH of the order of 3 kcal/mole over typical diffusion temperature ranges. This is large enough possibly to account for the presumed[22] curvature in the Arrhenius plot for self-diffusion in gold in terms of a monovacancy mechansim only.

In summary, a model calculation based on a Morse-like potential indicates that the frequencies of atomic vibrations in the vicinity of the defect vary with pressure in a way that is consistent with the observed temperature dependence of the activation volume for zinc. It is expected that more refined measurements for other metals would disclose the same type of behavior.

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Orthogonality Catastrophe in Metals

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The overlap of the ground states of a many-fermion system in the absence and presence of a localized potential is recalculated using a method introduced by Rivier and Simanek. Contrary to their claim, the result previously obtained by other methods is recovered.

The calculation of the overlap between the ground states of a fermion gas in the absence and the presence of a scattering potential is the simplest example of a class of related problems which contain infrared divergences.[1] Other examples occur in the problems of x-ray absorption in metals[2] and of magnetic impurities in metals.[3-5] In a recent Letter[6] Rivier and Simanek (RS) claim to have calculated an exact expression for the overlap which disagrees with that

given by the methods used in Refs. 1-5. We show here that their method, in fact, leads to the old result. Subtle difficulties which arise in calculating a key limit, not discussed by RS, necessitate a rather detailed presentation of the calculation.

The method of RS is similar to that of Nozières and De Dominicis (ND)[2] in that both calculate the fermion Green's function $\varphi(t,t')$ in the presence of a time-dependent contact (or separable) potential. RS consider the potential $\lambda V\theta(-t)e^{\eta t}$ and find the Fourier transform relative to the first argument of φ. (ND perform the entire calculation in the time domain.) The equation satisfied by $\varphi(\omega,t')$ is

$$\varphi(\omega,t')=g(\omega)e^{i\omega t'} -g(\omega)\lambda V\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi i}\frac{\varphi(\omega',t')}{\omega'-\omega+i\eta}, \tag{1}$$

which is equivalent to Eq. (8) of RS. The local free-fermion Green's function g is given by

$$g(\omega)=\int_{-\infty}^{\infty}d\epsilon\,\rho(\epsilon)(\omega-\epsilon-i\delta\,\mathrm{sgn}\epsilon)^{-1}, \tag{2}$$

where ρ is the density of states. The overlap is given by

$$\langle S\rangle=\exp[-\int_0^1 d\lambda\, V\int_{-\infty}^{0}dt\,e^{\eta t}\varphi(t,t^+)]. \tag{3}$$

The limit $\eta\to 0$ is to be taken to satisfy the requirement that the potential be turned on adiabatically. Equation (1) can be solved exactly in this limit, so the $\eta=0$ limit of φ is well defined. To determine whether Eq. (3) is well defined, we must examine how $\varphi(t,t^+)$ behaves in the limit $t\to-\infty$. From related studies,[4] we expect $\varphi(\eta=0)$ to approach a constant equal to the Green's function in a constant potential λV. This contribution to the t integral leads to a divergence as $\eta\to 0$, but it is purely imaginary and does not affect $|\langle S\rangle|$. We also expect a transient term in φ which decays away from the step change in the potential at $t=0$ and presumably is integrable. Finally, we have to consider the possibility that $\varphi(\eta\neq 0)$ contains a real term proportional to η as $t\to-\infty$. We have used perturbation theory on Eq. (1) to obtain the first-order correction to φ, and find that it does not contribute to Eq. (3).

To find $\varphi(\eta=0)$, let us introduce a new infinitesimal δ in Eq. (1) which is arbitrarily small and is to be distinguished from η. We introduce a function Φ which has a real-axis branch cut and is analytic elsewhere. The real-axis values are

$$\Phi^{\pm}(\omega)=(2\pi i)^{-1}\int_{-\infty}^{\infty}dx(x-\omega\mp i\delta)^{-1}\varphi(x,t'). \tag{4}$$

This allows us to express φ as

$$\varphi=\Phi^{+}-\Phi^{-}, \tag{5}$$

and Eq. (1) as

$$\varphi=ge^{i\omega t'}-\lambda Vg\Phi^{-}, \tag{6}$$

where the unwritten arguments are understood to be ω.[7] Another function with similar analytic properties must be constructed to satisfy

$$X^{+}/X^{-}=1-\lambda Vg, \tag{7}$$

and a suitable function is

$$X^{\pm}(\omega)=\exp\left\{(2\pi i)^{-1}\int_{-\infty}^{\infty}dx\,\frac{\ln[1-\lambda Vg(x)]}{x-\omega\mp i\delta}\right\}. \tag{8}$$

Eqs. (5)-(7) may be combined algebraically to yield

$$\Phi^{+}/X^{+}-\Phi^{-}/X^{-}=ge^{i\omega t'}/X^{+}. \tag{9}$$

A solution Φ which has the desired analytic properties and satisfies (9) is

$$\Phi^{\pm}(\omega)=\frac{X^{\pm}(\omega)}{2\pi i}\int_{-\infty}^{\infty}d\omega'\frac{g(\omega')e^{i\omega' t'}}{(\omega'-\omega\mp i\delta)X^{+}(\omega')} \tag{10}$$

The simplest expression for $\varphi(\omega,t')$ is obtained by substituting Eq. (10) in Eq. (6). The formal expression for the Fourier inversion is then substituted in Eq. (3). The order of the t and the ω integrals can be interchanged and the t integral performed, but *this procedure is well-defined only if we retain η as a finite quantity until after the ω Fourier-inversion integral is evaluated.* We obtain

$$\langle S\rangle=\exp\left\{\int_0^1 d\lambda\frac{V}{(2\pi)^2}\int_{-\infty}^{\infty}d\omega'\frac{g(\omega')}{X^{+}(\omega')}\int_{-\infty}^{\infty}d\omega\left[\frac{X^{+}(\omega)}{(\omega'-\omega-i\eta)(\omega'-\omega-i\delta)}-\frac{X^{-}(\omega)}{(\omega'-\omega-i\eta)(\omega'-\omega+i\delta)}\right]\right\}. \tag{11}$$

In the first term of the ω integral, the contour can be closed in the upper ω half-plane, and the result is zero. In the second term, it can be closed in the lower half-plane and picks up the residue at $\omega=\omega'-i\eta$, so

$$\langle S\rangle=\exp\left[\int_0^1 d\lambda\frac{V}{2\pi\eta}\int_{-\infty}^{\infty}d\omega'\frac{g(\omega')X^{-}(\omega'-i\eta)}{X^{+}(\omega')}\right]. \tag{12}$$

The $\eta = 0$ limit may now be taken using

$$\eta^{-1}X^{-}(\omega' - i\eta) \xrightarrow[\eta \to 0]{} \eta^{-1}X^{-}(\omega') - idX^{-}(\omega')/d\omega'. \quad (13)$$

The first term in Eq. (13) can easily be shown to yield the phase factor $\exp(i\Delta E/\eta)$, where ΔE is the energy shift produced by a constant potential V. The derivative is easily carried out because of the exponential form of X^{-}, and we find

$$|\langle S\rangle| = \exp\left\{-\int_0^1 d\lambda \frac{V}{(2\pi)^2}\int_{-\infty}^{\infty} d\omega' \tilde{g}(\omega') \times \int_{-\infty}^{\infty} dx \frac{\ln[1-\lambda V g(x)]}{(x-\omega'+i\delta)^2}\right\}, \quad (14)$$

where $\tilde{g} = g(1-\lambda V g)^{-1}$ is the Green's function in the presence of a constant potential λV.

The ω' integral in Eq. (14) may be carried out by substituting a spectral representation like Eq. (2) for $\tilde{g}$. Closing the contour in the lower ω' half-plane picks up the positive energy part of the $\tilde{g}$ spectrum only. The x integral may be simplified by introducing the retarded function g_r, which is given by keeping the denominator imaginary term in Eq. (2) positive for all energies. We can subtract $\ln[1-\lambda V g_r(x)]$ from the logarithm in Eq. (14) since its analyticity makes its integral zero. The resulting argument of the logarithm is unity for $x > 0$ and unimodular for $x < 0$, so

$$|\langle S\rangle| = \exp\{\pi^{-2}\int_0^1 d\lambda \int_0^{\infty} d\omega' \int_{-\infty}^{0} dx \times V[\mathrm{Im}\tilde{g}(\omega')]\delta_\lambda(x)(x-\omega')^{-2}\}, \quad (15)$$

where $\delta_\lambda(x)$ is the scattering phase shift produced by a constant potential λV:

$$\delta_\lambda(x) = \tan^{-1}\{-\lambda V \mathrm{Im}g(x)/[1-\lambda V \mathrm{Re}g(x)]\}. \quad (16)$$

We can adequately simulate discrete level spacing in a finite box by cutting off the low-energy end of the x and ω' integrations at $\Delta = \epsilon_F/N$, where N is the number of states of s-orbital symmetry. To evaluate the leading term, the nonsingular factors are set equal to their zero-energy limits. The x and ω' integrals then yield the factor $\ln(\Delta/\epsilon_F)$. The λ integral is trivial once we observe that $V\,\mathrm{Im}\tilde{g}(0^+)$ is equal to the λ derivative of $\delta_\lambda(0^-)$. The result for the overlap is, within a numerical constant,

$$|\langle S\rangle| = N^{-\gamma}, \quad \gamma \equiv \delta^2/2\pi^2, \quad (17)$$

where δ is the Fermi-surface phase shift for $\lambda = 1$.

This is precisely the result found by Anderson[3] and ND.[2] It is equally valid for all δ within the interval of width π accessible using the contact-interaction model. Unlike the previous derivations, the present method enables us in principle to evaluate the numerical constant by doing the x and ω integrals more accurately, after doing the λ integral analytically.[4]

In their analysis, RS did not distinguish the infinitesimal used in solving Eq. (1) from η. This renders limits such as Eq. (13) ambiguous and accounts, at least in part, for their failure to arrive at Eq. (17).

Note added in proof.—Similar corrections to Ref. 6 have also been found by Nozières.[8]

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