# Theory of the Range of Hot Electrons in Real Metals

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The equations of Quinn and Ferrell and of Quinn for the rate of energy loss of a hot electron in a free-electron gas are generalized to take solid-state effects into account. A general equation is derived, which in addition to a principal term which reduces to Quinn's result in the free-electron gas limit, contains terms which result from umklapp processes and local-field corrections. The additional terms are evaluated for aluminum on a one-OPW model and are found to result in a 16–30% decrease in the rate of energy loss. The effect of Fermi surface shape on the principal term is discussed in detail, with the aid of an exact recasting of the term into a form which explicitly shows its dependence on the equations of the energy surfaces. It is shown that nonspherical Fermi surfaces lead to an anisotropic hot-electron energy-loss rate, and that for certain shapes of Fermi surface the rate of energy loss is more singular than $(E_p-E_0)^3$ near the Fermi surface. It is found that the "flatter" the Fermi surface is, the greater is the rate of hot-electron energy loss. This is suggested as a possible explanation for the anomalously small hot-electron range observed in copper by Crowell *et al.*

## I. INTRODUCTION

THE problem of the range of hot electrons in metals has recently been of both experimental and theoretical interest. Experiments by Crowell *et al.*[1] and others[2] have determined the range of very low energy electrons in Pd, Cu, Ag, and Au. A theoretical treatment of the problem, using a dielectric constant approach, has been given by Quinn and Ferrell[3] and by Quinn.[4] Quinn[4] discusses the energy loss of electrons of energies within about 1 keV of the Fermi surface in a free-electron gas. He neglects solid-state effects, which would be expected to be important for electrons of such low energy, since the energy levels and/or wave functions of these electrons could not be well approximated by those for a free electron. In this paper the results of Quinn and Ferrell[3] and of Quinn[4] for the free-electron gas are generalized to a periodic lattice so as to take solid-state effects into account. Particular stress is laid on determining the effects of umklapp processes, of local-field corrections, and of Fermi surface shape on the range of electrons of energy very near the Fermi energy ($E\approx E_0$). All work is done using the random phase approximation (RPA) dielectric constant discussed by Ehrenreich and Cohen[5] and no attempt is made to include additional many-body effects. The electron-phonon interaction[6] is not considered in this paper. In other words, we restrict ourselves to considering that contribution to the energy loss of the hot electron which arises from the Coulomb interaction of the hot electron with the electrons of the lattice.

In Sec. II the equations of (A) for the rate of energy loss of a hot electron are generalized to the case of a solid. The result is an equation resembling Eq. (33) of (A), but containing terms arising from umklapp processes and from local-field effects. In Sec. III these terms are calculated on a one orthogonalized plane wave (OPW)[7] model, chosen because it is the simplest model for estimating effects arising from the presence of cores, which are neglected in a free-electron treatment. In the case of aluminum (a metal well described by the one-OPW model), it is found that the net effect of umklapp processes and local-field corrections, for a hot electron very close to the Al Fermi surface, is a decrease in the energy-loss rate in the range 16–30%. While the order of magnitude of the effect is probably correctly given by the crude estimate, the numerical values obtained should not be taken too seriously. The contribution of umklapp processes to plasmon creation is also estimated in Sec. III.

In Sec. IV umklapp and local-field effects are neglected, and the remaining expression for the rate of energy loss is recast into a form which shows its dependence on the shape of the energy surfaces. The rate of energy loss of electrons with energy $E\approx E_0$ is found to depend only on properties of the energy surfaces and electron wave functions at the Fermi energy, and is studied in detail for various shapes of Fermi surface. For a spherical Fermi surface the result of Quinn[4] for the free-electron gas, that $dE_p/dt\propto(E_p-E_0)^3$, is rederived. Nonspherical Fermi surfaces show an anisotropic absorption of hot electrons. It is shown that for a cylindrical Fermi surface the absorption is proportional to $(E_p-E_0)^3|\ln[(E_p-E_0)/E_0]|$, and that it is, in general, more singular than $(E_p-E_0)^3$ if the Fermi surface contains a straight-line segment, along which the normals to the surface are coplanar. This "flatness condition" is nearly fulfilled by the energy surfaces of Cu, and it is suggested that Fermi surface shape effects

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[1] C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. LaBate, Phys. Rev. **127**, 2006 (1962).
[2] References to experimental work prior to 1962 may be found in Crowell *et al.* (reference 1).
[3] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958). This paper is hereafter referred to as (A).
[4] J. J. Quinn, Phys. Rev. **126**, 1453 (1962).
[5] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).
[6] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), Chap. VII, p. 268.
[7] *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, pp. 367–411.

may account for the abnormally large attenuation of hot electrons observed[1] in Cu.

## II. GENERAL THEORY

In this section we generalize the results derived in (A) for the rate of energy loss of a hot electron in a free-electron gas. Many steps are precisely the same as in (A) and the reader is referred to that paper for details. Throughout the paper we take $\hbar=c=1$. As shown by Quinn[4] and by Engelsberg,[8] the rate of energy loss is obtained by appropriately inserting an energy factor in the integrand of an expression for the imaginary part of the electron self-energy. According to the usual Feynman rules,[9] the self-energy of an electron of momentum $\mathbf{p}$, energy $E_p$, and wave function $\psi_p(\mathbf{x})$ in the crystal is given by

$$E_{\text{self}}=e^2T^{-1}\int\int d\mathbf{x}_1dt_1d\mathbf{x}_2dt_2\,\psi_p(\mathbf{x}_1)\psi_p^*(\mathbf{x}_2)\times\exp[iE_p(t_2-t_1)]K_+(2,1)G_+(2,1). \quad (1)$$

Here $G_+(2,1)$ is the photon propagator in the crystal, $K_+(2,1)$ is the electron propagator, and the time integrals extend from $-T/2$ to $T/2$. Just as in the case treated in (A), the electron propagator is given by

$$K_+(2,1)=\int d\mathbf{k}\int_{-\infty}^{\infty}d\omega\,\frac{V}{(2\pi)^4}\,\frac{i}{\omega-E_k(1-i\delta)}\psi_k(\mathbf{x}_2)\psi_k^*(\mathbf{x}_1)\times\exp[-i\omega(t_2-t_1)],\quad \delta>0. \quad (2)$$

The wave function $\psi_k(\mathbf{x})$ and energy $E_k$ are no longer the free-electron wave function and energy, but are the band-theoretic wave function and energy of the electron in the lattice, labeled by $\mathbf{k}$ according to an extended zone scheme.[10] The wave functions are normalized to 1 in the volume $V$ of the crystal and the $\mathbf{k}$ integration extends over all of $\mathbf{k}$ space.

The photon propagator $G_+(2,1)$ is defined as the positive frequency part (for $t_2-t_1>0$) of $G(2,1)$, where $G(2,1)$ relates the charge density $\rho(\mathbf{x}_1,t_1)$ at time $t_1$ to the potential $\phi(\mathbf{x}_2,t_2)$ which the charge induces at time $t_2$ according to

$$\phi(\mathbf{x}_2,t_2)=\int d\mathbf{x}_1dt_1\,G(2,1)\rho(\mathbf{x}_1,t_1). \quad (3)$$

Let us Fourier transform $\phi(\mathbf{x},t)$ and $\rho(\mathbf{x},t)$ according to

$$\begin{Bmatrix}\phi(\mathbf{x},t)\\ \rho(\mathbf{x},t)\end{Bmatrix}=\sum_{\mathbf{K}}\int_{B_1}d\mathbf{q}\,e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}\int_{-\infty}^{\infty}d\omega\,e^{-i\omega t}\begin{Bmatrix}\phi(\mathbf{q},\mathbf{K},\omega)\\ \rho(\mathbf{q},\mathbf{K},\omega)\end{Bmatrix}.$$

The vectors $\mathbf{K}$ are reciprocal-lattice vectors and the integration over $\mathbf{q}$ extends only over the first Brillouin zone of $\mathbf{q}$ space. It is easy to show that $\phi(\mathbf{q},\mathbf{K},\omega)$ and $\rho(\mathbf{q},\mathbf{K},\omega)$ are related according to[11]

$$\phi(\mathbf{q},\mathbf{K},\omega)=4\pi|\mathbf{q}+\mathbf{K}|^{-2}\times\sum_{\mathbf{K}''}\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)\rho(\mathbf{q}+\mathbf{K}'',\,\omega), \quad (4)$$

where $\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)$ is defined implicitly by the three equations:

$$\sum_{\mathbf{K}''}\epsilon(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)\epsilon^{-1}(\mathbf{q}+\mathbf{K}'',\,\mathbf{q}+\mathbf{K}',\,\omega)=\delta_{\mathbf{K},\mathbf{K}'}, \quad (5)$$

$$\epsilon(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)=\delta_{\mathbf{K},\mathbf{K}''}-|\mathbf{q}+\mathbf{K}''|^{-2}G(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega), \quad (6)$$

and

$$G(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)=\frac{e^2}{\pi^2}\int d\mathbf{k}\sum_{\mathbf{K}'}\frac{\langle\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle\langle\mathbf{k}+\mathbf{q}+\mathbf{K}'|e^{i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}}|\mathbf{k}\rangle[f_0(E_k)-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})]}{\omega+E_k-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}}. \quad (7)$$

In Eq. (7), $f_0(E)$ is the Fermi-Dirac distribution function, normalized to the total number of electrons in the crystal; the matrix elements are defined by

$$\langle\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}|\mathbf{k}'\rangle\equiv\int d\mathbf{x}\,\psi_k^*(\mathbf{x})e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}\psi_{k'}(\mathbf{x}),$$

and the $\omega$ appearing in the denominator is understood to have a small positive imaginary part. From Eqs. (3) and (4) and the requirement that $G_+(2,1)$ contain only positive frequencies for $t_{21}=t_2-t_1>0$, we find that

$$G_+(2,1)=\frac{4\pi}{(2\pi)^4}\int_{B_1}d\mathbf{q}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\int_C d\omega\,\frac{\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)}{|\mathbf{q}+\mathbf{K}|^2}e^{i\mathbf{q}\cdot\mathbf{x}_{21}-i\omega t_{21}}e^{i\mathbf{K}\cdot\mathbf{x}_2}e^{-i\mathbf{K}''\cdot\mathbf{x}_1}, \quad (8)$$

where the contour $C$ is the same as in (A). The self-energy is obtained by inserting the expressions for $G_+$ and $K_+$ into Eq. (1) and evaluating the integrals. The manipulations are precisely the same as those in (A); the result is

[8] S. Engelsberg, Phys. Rev. **123**, 1130 (1961); **126**, 1262 (1962).
[9] R. P. Feynman, Phys. Rev. **76**, 769 (1949).
[10] N. F. Mott and H. Jones (reference 6), pp. 62–63.
[11] S. L. Adler, Phys. Rev. **126**, 413 (1962).

$E_{\text{self}}=E_{\text{residue}}+E_{\text{line}}$, with

$$E_{\text{residue}}=4\pi e^2\int_{E_0<E_{\mathbf{p}-\mathbf{q}}<E_{\mathbf{p}}}\frac{d\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\frac{\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})}{|\mathbf{q}+\mathbf{K}|^2}M^*(\mathbf{q},\mathbf{K}'')M(\mathbf{q},\mathbf{K}),\tag{9}$$

and

$$E_{\text{line}}=-\frac{4\pi e^2}{(2\pi)^4}\int d\mathbf{q}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\int_{-\infty}^{\infty}d\eta\,\frac{\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,i\eta)(E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})}{[\eta^2+(E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})^2]|\mathbf{q}+\mathbf{K}|^2}M^*(\mathbf{q},\mathbf{K}'')M(\mathbf{q},\mathbf{K}).\tag{10}$$

We have introduced the abbreviation $M(\mathbf{q},\mathbf{K})\equiv\langle\mathbf{p}|\exp[i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}-\mathbf{q}\rangle$, the $\mathbf{p}$ dependence not being indicated explicitly. To obtain the rate of energy loss we need only find the imaginary part of $E_{\text{self}}$. From Eqs. (5), (6), and (7) defining $\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)$, it is straightforward to verify the symmetry $\epsilon^{-1}(-\mathbf{q}-\mathbf{K},\,-\mathbf{q}-\mathbf{K}'',\,i\eta)^*=\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,i\eta)$. Using time-reversal symmetry, which implies that

$$\langle-\mathbf{k}|\exp[i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}]|-\mathbf{k}-\mathbf{q}-\mathbf{K}'\rangle=\langle\mathbf{k}+\mathbf{q}+\mathbf{K}'|\exp[i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}]|\mathbf{k}\rangle,$$

it is easy to demonstrate that

$$|\mathbf{q}+\mathbf{K}''|^{-2}\epsilon^{-1}(\mathbf{q}+\mathbf{K}'',\,\mathbf{q}+\mathbf{K},\,i\eta)=|\mathbf{q}+\mathbf{K}|^{-2}\epsilon^{-1}(-\mathbf{q}-\mathbf{K},\,-\mathbf{q}-\mathbf{K}'',\,i\eta).$$

From these two symmetries we find

$$[\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,i\eta)|\mathbf{q}+\mathbf{K}|^{-2}]^*=\epsilon^{-1}(\mathbf{q}+\mathbf{K}'',\,\mathbf{q}+\mathbf{K},\,i\eta)|\mathbf{q}+\mathbf{K}''|^{-2},$$

from which it follows immediately that $E_{\text{line}}{}^*=E_{\text{line}}$, or $\text{Im}E_{\text{line}}=0$. The self-energy of an isolated electron, $E_{\text{free}}$, which must be subtracted to renormalize $E_{\text{self}}$, is purely real. Thus, the sole contribution to $\text{Im}E_{\text{self}}$ comes from $E_{\text{residue}}$. According to Quinn[4] and to Engelsberg,[8] the rate of energy loss of the hot electron is obtained by inserting a factor $2[E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}}]$ in the integrand of Eq. (10). Thus, we obtain finally for the rate of energy loss of the hot electron,

$$dE_{\mathbf{p}}/dt=\frac{e^2}{\pi^2}\int_{E_0<E_{\mathbf{p}-\mathbf{q}}<E_{\mathbf{p}}}d\mathbf{q}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\frac{\text{Im}\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})}{|\mathbf{q}+\mathbf{K}|^2}(E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})M^*(\mathbf{q},\mathbf{K}'')M(\mathbf{q},\mathbf{K}).\tag{11}$$

Equation (11) is the starting point of the detailed investigations to be described in this paper.

It is helpful first to discuss Eq. (11) qualitatively and to list the main effects which one would expect to see in a solid which do not appear in the free-electron gas problem treated by Quinn. The term of Eq. (11) with $\mathbf{K}=\mathbf{K}''=0$ is the analog of the free-electron gas expression, but deviates from it in several respects:

(1) Instead of $\epsilon(\mathbf{q},\mathbf{q},\omega)^{-1}$, the local-field corrected dielectric constant[11] $\epsilon^{-1}(\mathbf{q},\mathbf{q},\omega)$ appears.

(2) There appears the factor $|\langle\mathbf{p}-\mathbf{q}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{p}\rangle|^2$. This factor is smaller than 1, corresponding to the fact that the hot electron is not always attenuated without transfer of momentum to the translational motion of the lattice.

(3) The energies and wave functions which determine $\epsilon^{-1}(\mathbf{q},\mathbf{q},\omega)$ according to Eqs. (5)–(7) are not free-electron energies and wave functions; this has a strong effect on the hot-electron range.

The third of these effects is discussed in more detail in Sec. IV.

The terms of Eq. (11) with $\mathbf{K}\neq0$ or $\mathbf{K}''\neq0$ do not appear in the free-electron case. They can be divided into two classes:

(1) Those with $\mathbf{K}''=\mathbf{K}\neq0$ correspond to umklapp processes, in which momentum $\mathbf{K}$ (say) is given to translational motion of the lattice, the process occurring with weight $|\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle|^2$. These terms clearly add to the rate of energy loss.

(2) The terms with $\mathbf{K}''\neq\mathbf{K}$ would not appear were it not for local-field corrections to the dielectric constant,[11] which cause the $\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K}'',\,\omega)$ with $\mathbf{K}''\neq\mathbf{K}$ to be nonvanishing. These terms may be regarded as a composite effect of local-field corrections and of umklapp processes. It is not obvious from inspection whether they increase or decrease the rate of energy loss of a hot electron.

The sum of the terms with $\mathbf{K}\neq0$ or $\mathbf{K}''\neq0$ is estimated in Sec. III.

Let us note, finally, that in the limit when the hot-electron energy $E_{\mathbf{p}}$ becomes much larger than the typical orbital electron energy of a rydberg, the states $\psi_{\mathbf{p}}(\mathbf{x})$ and $\psi_{\mathbf{p}-\mathbf{q}}(\mathbf{x})$ are very nearly plane wave states over most of the region of the $\mathbf{q}$ integration. In this case,

$$M^*(\mathbf{q},\mathbf{K}'')M(\mathbf{q},\mathbf{K})\approx\delta_{\mathbf{K}'',0}\delta_{\mathbf{K},0}$$

and the umklapp and umklapp-local-field terms drop out. Thus, these terms have essentially no effect on the well-known formulas for the stopping power of materials for fast electrons.[12]

[12] *Experimental Nuclear Physics*, edited by E. Segrè (John Wiley & Sons, Inc., New York, 1953), Vol. I, Part II, Sec. 2.

## III. UMKLAPP AND UMKLAPP-LOCAL-FIELD EFFECTS

In this section we discuss in detail the effect on the hot-electron range of the terms in Eq. (11) with $\mathbf{K}$ or $\mathbf{K}''$ unequal to zero. To see why the sum of these terms must be carefully estimated, let us consider the sum of the weighting coefficients of those terms with $\mathbf{K}=\mathbf{K}''$:

$$\sum_{\mathbf{K}\neq 0}|\langle \mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle|^2$$
$$=\int d\mathbf{x}d\mathbf{x}'\,\psi_{\mathbf{p}-\mathbf{q}}^*(\mathbf{x})\psi_{\mathbf{p}-\mathbf{q}}(\mathbf{x}')\psi_{\mathbf{p}}(\mathbf{x})\psi_{\mathbf{p}}^*(\mathbf{x}')\exp[-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')]\sum_{\mathbf{K}}\exp[-i\mathbf{K}\cdot(\mathbf{x}-\mathbf{x}')]-|\langle \mathbf{p}-\mathbf{q}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{p}\rangle|^2$$
$$=V_a^{-1}\int_0 d\mathbf{x}\,|u_{\mathbf{p}-\mathbf{q}}(\mathbf{x})|^2|u_{\mathbf{p}}(\mathbf{x})|^2-|\langle \mathbf{p}-\mathbf{q}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{p}\rangle|^2\approx V_a^{-1}\int_0 d\mathbf{x}\,|u_{\mathbf{p}}(\mathbf{x})|^4-1. \quad (12)$$

Here $V_a$ is the unit cell volume, the subscript 0 indicates integration over the unit cell, and $u_{\mathbf{p}}(\mathbf{x})$ is the cell periodic part of $\psi_{\mathbf{p}}(\mathbf{x})$: $\psi_{\mathbf{p}}(\mathbf{x})=V^{-1/2}\exp(i\mathbf{p}\cdot\mathbf{x})u_{\mathbf{p}}(\mathbf{x})$. To gain an idea of the magnitude of the integral in Eq. (12), we use the Schwartz inequality in the form,

$$\int_P d\mathbf{x}\,|u_{\mathbf{p}}(\mathbf{x})|^4\geqslant\left[\int_P d\mathbf{x}\,x^{-1}|u_{\mathbf{p}}(\mathbf{x})|^2\right]^2\left[\int_P d\mathbf{x}\,x^{-2}\right]^{-1},$$

where the integrals are taken over an atomic polyhedron containing an atom at $\mathbf{x}=0$. Then $\int_P d\mathbf{x}\,x^{-2}=4\pi r_P$, where $r_P$ is the mean atomic polyhedron radius, and $\int_P d\mathbf{x}\,|u_{\mathbf{p}}(\mathbf{x})|^2x^{-1}\equiv V_P/r_c$, where $V_P$ is the atomic polyhedron volume. We may regard the $r_c$ so defined as an average core radius since the periodic part $u_{\mathbf{p}}(\mathbf{x})$ is largest in the core region. Thus, we have

$$V_a^{-1}\int_0 d\mathbf{x}\,|u_{\mathbf{p}}(\mathbf{x})|^4\approx V_P^{-1}\int_P d\mathbf{x}\,|u_{\mathbf{p}}(\mathbf{x})|^4 \gtrsim\tfrac{1}{3}(r_P/r_c)^2. \quad (13)$$

In metals in which the core diameter is smaller than the diameter of the atomic polyhedron, which is usually the case, $(r_P/r_c)^2>1$ and the sum of the weighting coefficients of Eq. (12) is of order unity. Thus, if apart from the weighting coefficients $|M(\mathbf{q},\mathbf{K})|^2$, all of the umklapp terms made to the $\mathbf{q}$ integration in Eq. (11) a contribution roughly equal to the contribution of the $\mathbf{K}=\mathbf{K}''=0$ term, their net effect, when summed up, would be to increase significantly the rate of energy loss. So we must clearly examine carefully how many $\mathbf{K}$ values actually contribute appreciably.

To do this we use a one-OPW[7] model for the valence electron wave functions and energy levels, this being the simplest model which takes into account the largeness of the wave functions in the core region. Since the one-OPW model accounts quite well for the valence electron properties of aluminum,[13] the calculations will be done explicitly for the case of this metal. The model will be used only for calculating approximate estimates of the matrix elements; in performing the various integrations involved in evaluating the hot-electron attenuation the matrix elements will be treated as constants. The one-OPW wave function for a valence electron of momentum $\mathbf{k}$ in Al is given in Appendix I, along with numerical values of its various parameters. The energy surfaces in Al are nearly equal to the free-electron surfaces ($E_{\mathbf{k}}\approx k^2/2m$) over most of the Brillouin zone.

The first step is to calculate approximate expressions for the components $\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)$ of the inverse dielectric constant. We will treat the off-diagonal components, $\epsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)$, $\mathbf{K}''\neq\mathbf{K}$ as small perturbations compared to the diagonal components $\epsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K},\omega)$. Then first-order perturbation theory gives

$$\begin{aligned}&\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K},\omega)\approx\epsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K},\omega)^{-1},\\&\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)\approx\epsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K},\omega)^{-1}\\&\qquad\times G(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)|\mathbf{q}+\mathbf{K}''|^{-2}\\&\qquad\times\epsilon(\mathbf{q}+\mathbf{K}'',\mathbf{q}+\mathbf{K}'',\omega)^{-1}.\end{aligned} \quad (14)$$

Some further approximations on $\epsilon^{-1}$ are necessary in order to make the calculation tractable. We remark that by completeness of the $u_{\mathbf{k}}$,

$$\sum_{\mathbf{K}''\neq\mathbf{K}}|\langle\mathbf{k}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2 =1-|\langle\mathbf{k}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{k}+\mathbf{q}+\mathbf{K}\rangle|^2. \quad (15)$$

In the one-OPW model,

$$|\langle\mathbf{k}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{k}+\mathbf{q}+\mathbf{K}\rangle|^2\approx 1,$$

implying that the left-hand side of Eq. (15) is much smaller than one. Consequently, in the expression of Eq. (7) for $G(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)$ we neglect all terms which are quadratic in matrix elements of the type $\langle\mathbf{k}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle$, $\mathbf{K}'\neq\mathbf{K}$. This gives[14]

$$\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K},\omega)\approx\epsilon_F(\mathbf{q}+\mathbf{K},\omega)^{-1}, \quad (16)$$

[13] W. A. Harrison, Phys. Rev. **116**, 555 (1959); **118**, 1182 (1960); B. Segall, *ibid.* **124**, 1797 (1961).

[14] Core screening effects are negligible: The core polarizability $\alpha_c$ is roughly equal to $nV_c$, where $V_c$ is the core volume and $n=V_P^{-1}$ is the number of cores per unit volume. Thus, $\alpha=(r_c/r_P)^3\ll 1$.

and

$$G(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)\approx\frac{e^2}{\pi^2}\int d\mathbf{k}\,\frac{\langle\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}\rangle\langle\mathbf{k}+\mathbf{q}+\mathbf{K}|e^{i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}}|\mathbf{k}\rangle[f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}})]}{\omega+E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}}}$$
$$+\frac{e^2}{\pi^2}\int d\mathbf{k}\,\frac{\langle\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}''\rangle\langle\mathbf{k}+\mathbf{q}+\mathbf{K}''|e^{i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}}|\mathbf{k}\rangle[f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}''})]}{\omega+E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}''}},\quad(17)$$

where $\epsilon_F$ denotes the free-electron gas dielectric constant calculated by Lindhard. The formula for $\epsilon_F$ is given in Appendix II. Inserting Eqs. (16) and (17) into Eq. (11) and making a change of variable in the second term of Eq. (17) leads to

$$\frac{dE_\mathbf{p}}{dt}=\frac{e^2}{\pi^2}\int_{E_0<E_{\mathbf{p}-\mathbf{q}}<E_\mathbf{p}}d\mathbf{q}\,[E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}}][K(\mathbf{p},\mathbf{q})+D(\mathbf{p},\mathbf{q})+F(\mathbf{p},\mathbf{q})]\quad(18)$$

with

$$K(\mathbf{p},\mathbf{q})=\mathrm{Im}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\frac{\epsilon_F^{-1}(\mathbf{q}+\mathbf{K},\omega)\epsilon_F^{-1}(\mathbf{q}+\mathbf{K}'',\omega)}{|\mathbf{q}+\mathbf{K}|^2|\mathbf{q}+\mathbf{K}''|^2}\frac{e^2}{\pi^2}$$
$$\times\int d\mathbf{k}\,\frac{2\,\mathrm{Re}[R(\mathbf{q},\mathbf{k},\mathbf{K},\mathbf{K}'')M(\mathbf{q},\mathbf{K})M^*(\mathbf{q},\mathbf{K}'')][f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}})]}{\omega+E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}}},\quad(19)$$

and

$$D(\mathbf{p},\mathbf{q})=\mathrm{Im}\sum_{\mathbf{K}\neq0}\frac{\epsilon_F^{-1}(\mathbf{q}+\mathbf{K},\omega)|M(\mathbf{q},\mathbf{K})|^2}{|\mathbf{q}+\mathbf{K}|^2}.\quad(20)$$

The free-electron gas kernel $F(\mathbf{p},\mathbf{q})$, which arises from the $\mathbf{K}=\mathbf{K}''=0$ term of Eq. (11), is given by

$$F(\mathbf{p},\mathbf{q})=\mathrm{Im}\epsilon^{-1}(\mathbf{q},\omega)q^{-2}|M(\mathbf{q},0)|^2.\quad(21)$$

In writing Eqs. (19) and (20), we have made use of the definition

$$R(\mathbf{q},\mathbf{k},\mathbf{K},\mathbf{K}'')=\langle\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}\rangle\langle\mathbf{k}+\mathbf{q}+\mathbf{K}|e^{i(\mathbf{q}+\mathbf{K}'')\cdot\mathbf{x}}|\mathbf{k}\rangle.\quad(22)$$

In order to make the calculation tractable, we replace $2\,\mathrm{Re}[R(\mathbf{q},\mathbf{k},\mathbf{K},\mathbf{K}'')M(\mathbf{q},\mathbf{K})M^*(\mathbf{q},\mathbf{K}'')]$ by an appropriate average over $\mathbf{k}$. This gives

$$K(\mathbf{p},\mathbf{q})=\mathrm{Im}\sum_{\mathbf{K}}\sum_{\mathbf{K}''}\frac{\epsilon_F^{-1}(\mathbf{q}+\mathbf{K},\omega)\epsilon_F^{-1}(\mathbf{q}+\mathbf{K}'',\omega)}{|\mathbf{q}+\mathbf{K}|^2|\mathbf{q}+\mathbf{K}''|^2}\langle 2\,\mathrm{Re}RMM^*\rangle_{\mathrm{avk}}G_F(\mathbf{q}+\mathbf{K},\omega).\quad(23)$$

Let us only consider hot electrons very close to the Fermi surface, that is, with $E_\mathbf{p}\approx E_0$. Then it is an excellent approximation to replace $|\epsilon_F(\mathbf{q},\omega)|^2$ in the denominators by $|\epsilon_{F1}(\mathbf{q},0)|^2\approx(1+k_s^2/q^2)^2$, where $k_s$ is the reciprocal Thomas-Fermi screening length. Using the Lindhard result in an approximation valid for small $\omega$,

$$\epsilon_{F2}(\mathbf{q},\omega)=\frac{\Lambda\theta(2k_0-q)}{q^3},\quad\Lambda=\frac{3\omega_p^2}{v_0^2}\frac{\pi}{2}\frac{\omega}{v_0},\quad\begin{aligned}\theta(x)&=1,\quad x>0,\\&=0,\quad x<0.\end{aligned}$$

($v_0$ is the Fermi velocity, $k_0$ is the Fermi momentum, and $\omega_p$ is the plasma frequency), we find that $K(\mathbf{p},\mathbf{q})=A(\mathbf{p},\mathbf{q})+B(\mathbf{p},\mathbf{q})+C(\mathbf{p},\mathbf{q})$ with

$$A(\mathbf{p},\mathbf{q})=\sum_{\mathbf{K}\neq0}\langle 2\,\mathrm{Re}R(\mathbf{q},\mathbf{k},0,\mathbf{K})M(\mathbf{q},0)M^*(\mathbf{q},\mathbf{K})\rangle_{\mathrm{avk}}\frac{\Lambda}{(k_s^2+q^2)(k_s^2+|\mathbf{q}+\mathbf{K}|^2)}$$
$$\times\left\{\frac{\theta(2k_0-|\mathbf{q}+\mathbf{K}|)k_s^2}{|\mathbf{q}+\mathbf{K}|(k_s^2+|\mathbf{q}+\mathbf{K}|^2)}-\frac{q\theta(2k_0-q)}{k_s^2+q^2}\right\},$$
$$B(\mathbf{p},\mathbf{q})=\sum_{\mathbf{K}\neq0}\langle 2\,\mathrm{Re}R(\mathbf{q},\mathbf{k},\mathbf{K},0)M(\mathbf{q},\mathbf{K})M^*(\mathbf{q},0)\rangle_{\mathrm{avk}}\frac{\Lambda}{(k_s^2+|\mathbf{q}+\mathbf{K}|^2)(k_s^2+q^2)}$$
$$\times\left\{\frac{\theta(2k_0-q)k_s^2}{q(k_s^2+q^2)}-\frac{|\mathbf{q}+\mathbf{K}|\theta(2k_0-|\mathbf{q}+\mathbf{K}|)}{k_s^2+|\mathbf{q}+\mathbf{K}|^2}\right\},\quad(24)$$

$$C(\mathbf{p},\mathbf{q})=\sum_{0\neq\mathbf{K}\neq\mathbf{K}''\neq 0}\sum\langle 2\,\mathrm{Re}R(\mathbf{q},\mathbf{k},\mathbf{K},\mathbf{K}'')M(\mathbf{q},\mathbf{K})M^*(\mathbf{q},\mathbf{K}'')\rangle_{\mathrm{avk}}\frac{\Lambda}{(k_s^2+|\mathbf{q}+\mathbf{K}|^2)(k_s^2+|\mathbf{q}+\mathbf{K}''|^2)}$$
$$\times\left\{\frac{\theta(2k_0-|\mathbf{q}+\mathbf{K}''|)k_s^2}{|\mathbf{q}+\mathbf{K}''|(k_s^2+|\mathbf{q}+\mathbf{K}''|^2)}-\frac{|\mathbf{q}+\mathbf{K}|\theta(2k_0-|\mathbf{q}+\mathbf{K}|)}{k_s^2+|\mathbf{q}+\mathbf{K}|^2}\right\}.$$

We also find, by use of Eq. (16), that

$$D(\mathbf{p},\mathbf{q})=-\sum_{\mathbf{K}\neq 0}\frac{|M(\mathbf{q},\mathbf{K})|^2\Lambda\theta(2k_0-|\mathbf{q}+\mathbf{K}|)}{|\mathbf{q}+\mathbf{K}|(k_s^2+|\mathbf{q}+\mathbf{K}|^2)^2}.$$

To get an explicit expression for the hot-electron attenuation we must make several more approximations. First, we note from the expressions for the one-OPW matrix elements in Appendix I that the quantities $M(\mathbf{q},\mathbf{K})$, $M^*(\mathbf{q},\mathbf{K}'')$, and $R(\mathbf{q},\mathbf{k},\mathbf{K},\mathbf{K}'')$ are all real, and for small $\mathbf{K}$ and $\mathbf{K}''$ are all negative. For larger $\mathbf{K}$, $M(\mathbf{q},\mathbf{K})$ becomes positive and then tends to zero. Since the factors multiplying the matrix elements are largest for small $\mathbf{K}$ and $\mathbf{K}''$, we replace $M$, $M^*$, and $R$ by negative constants in evaluating the sums over $\mathbf{K}$ and $\mathbf{K}''$ and cut off the sums at values of $\mathbf{K}$ and $\mathbf{K}''$ at which the matrix elements are still negative. To try to be a little less crude, we actually use two cutoffs and two constants, corresponding to the $2s,p$ and $1s$ core orbital contributions to the matrix elements. The sums over $\mathbf{K}$ and $\mathbf{K}''$ are then replaced by integrals, and finally the $\mathbf{q}$ integration is performed. The results of these manipulations may be expressed in the form of ratios (the expression for $F$, the rate of energy loss in a free electron gas, is given in Appendix II):

$$\begin{aligned}(A+B)/D&=4\gamma^2(1+\gamma^2)\\&\quad\times[-2\alpha\gamma(1+\gamma^2)^{-1}+\beta\ln(1+\gamma^{-2})],\\C/D&=(2MV_ak_s^3/\pi^2)\alpha\beta(1+\gamma^2),\\\frac{D}{F}&=|M|^2\frac{V_a}{\pi^2}k_0^3\frac{2\gamma(1+\gamma^2)^{-1}}{\gamma(1+\gamma^2)^{-1}+\tan^{-1}(\gamma^{-1})},\\\alpha&=\tfrac{1}{2}[(\lambda_2/2k_s)-\tan^{-1}(\lambda_2/2k_s)\\&\quad+(\lambda_1/2k_s)-\tan^{-1}(\lambda_1/2k_s)],\\\beta&=\tfrac{1}{2}\ln(1+\gamma^{-2})-(1+\gamma^2)^{-1},\\\gamma&=k_s/2k_0.\end{aligned}\tag{25}$$

The two terms in $\alpha$ are, respectively, the $2s$, $p$, and $1s$ orbital contributions, with $2s$, $p$, and $1s$ cutoffs of $\lambda_2/2$ and $\lambda_1/2$. Numerical evaluation of these formulas, using the value $M^2\approx 0.02$ estimated in Appendix I, gives

$$\begin{aligned}(A+B)/D&=-3.7,\\C/D&=0.85,\\D/F&=0.16.\end{aligned}\tag{26}$$

Thus $(A+B+C+D)/F=-0.30$. If the cutoffs are taken as $\lambda_2/3$ and $\lambda_1/3$ instead of $\lambda_2/2$ and $\lambda_1/2$, the effect is reduced to $(A+B+C+D)/F=-0.16$. Thus, assuming the validity of the model used and the approximations made, the combined effect of the umklapp and the umklapp-local-field terms is to decrease the hot-electron energy-loss rate by 16–30%. Since the approximations made are quite crude and especially since the small value of $C$ results from the near cancellation of two terms which are considerably larger, the numerical results of Eq. (26) should be treated with some skepticism. However, certain semiquantitative conclusions can be reasonably drawn from the model calculation:

(1) The absolute value of the sum of terms $A+B+C$ is of the same order of magnitude as $D$ ($A+B+C\approx -2.6D$);

(2) The net correction to the hot-electron attenuation resulting from the umklapp and umklapp-local-field terms, in the one-OPW model,[15] is not large and is probably of order 30% or smaller;

(3) This correction does not necessarily lead to an increase in the attenuation, as would be obtained if only the umklapp term $D$ were kept. It is clear that the sum of umklapp-local-field terms $A+B+C$ is more than capable of cancelling the positive contribution from $D$.

It is also of interest to determine the effect of umklapp processes and of umklapp-local-field effects on the plasmon creation probability. Near the plasmon pole the perturbation theory expressions of Eq. (14) for the off-diagonal components of $\epsilon^{-1}$ are not valid. Consequently, let us restrict ourselves to obtaining an estimate of the umklapp contribution to the plasmon creation rate, *neglecting all local-field corrections*. Using $\epsilon_F(\mathbf{q},\omega)\approx(1-\omega_p^2/\omega^2)+i\epsilon_{F2}$, an approximate expression valid near the plasmon pole, we find for the umklapp contribution,

$$D'=-\frac{e^2}{\pi^2}\int_{E_0<E_{\mathbf{p}-\mathbf{q}}<E_{\mathbf{p}}}d\mathbf{q}\sum_{\mathbf{K}}\frac{\delta[1-\omega_p^2/(E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})^2](E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}})|M|^2}{|\mathbf{q}+\mathbf{K}|^2}\theta\left(\frac{E_{\mathbf{p}}-E_{\mathbf{p}-\mathbf{q}}}{|\mathbf{q}+\mathbf{K}|V_0}-\frac{|\mathbf{q}+\mathbf{K}|}{2k_0}-1\right).\tag{27}$$

The step function $\theta$ expresses the condition that $\epsilon_{F2}$ must vanish for there to be a plasmon pole. Let us consider $|\mathbf{p}|\approx\lambda_1/3$, the value for which the largest number of umklapp processes would be expected to contribute. In

[15] By using a one-OPW model we have calculated a "minimal" effect common to all solids and arising from the presence of the cores. Appreciable mixing of OPW's could lead to certain of the matrix elements $M$ being much larger than the estimate obtained using the one-OPW model, and might lead to a larger umklapp and umklapp-local-field effect.

this region, only the $1s$ core orbital contributes appreciably to $M(\mathbf{q},\mathbf{K})$. Approximating $M(\mathbf{q},\mathbf{K})$ by a constant, replacing the sum over $\mathbf{K}$ by an integral and carrying out the $\mathbf{K}$ and $\mathbf{q}$ integrations leads to a simple result, which may be expressed as the ratio of $D'$ to the rate of energy loss by plasmon creation in a free electron gas, $F'$ (the expression for $F'$ is given in Appendix II):

$$\frac{D'}{F'}=\frac{V_a}{2\pi^2}M_s{}^2\frac{2p\mu(\nu-k_0)}{\ln[(\nu-k_0)/(p-\mu)]}, \tag{28}$$

$$\nu=(k_0{}^2+2m\omega_p)^{1/2},\quad \mu=(p^2-2m\omega_p)^{1/2},\quad p=|\mathbf{p}|.$$

Numerical evaluation in the case of Al, for $p\approx 4k_0$, gives $D'/F'=0.37$, greater than in the low-energy case treated above. Of course, in order to obtain the total deviation from the free-electron gas plasmon creation rate, local-field corrections would have to be taken into account. What is important to note here is that at certain energies, in order to calculate the plasmon creation rate to better than 40%, umklapp and umklapp-local-field effects must be considered.

## IV. FERMI SURFACE SHAPE EFFECTS

In this section we discuss changes in the value of the $\mathbf{K}=\mathbf{K}''=0$ term of Eq. (11) which result from solid-state effects. Since this term is the principal contribution to the hot-electron attenuation, careful study of it is warranted. Let us first consider the case of a one-OPW metal. As we saw in the last section, we then have

$$\epsilon^{-1}(\mathbf{q}+\mathbf{K},\,\mathbf{q}+\mathbf{K},\,\omega)\approx\epsilon_F(\mathbf{q}+\mathbf{K},\,\omega)^{-1}$$

and

$$|\langle\mathbf{p}-\mathbf{q}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{p}\rangle|^2\approx 1.$$

Thus, in the one-OPW case the $\mathbf{K}=\mathbf{K}''=0$ term has nearly the same value as in the case of a free-electron gas. In other words, it is not appreciably affected by the addition of core orthogonalization terms to the free-electron gas wave function.

Large changes do appear, however, when the energy surfaces and electron wave functions differ appreciably from those of a free electron. To make the dependence of the hot-electron absorption on the function $E_\mathbf{k}$ more apparent, let us cast the $\mathbf{K}=\mathbf{K}''=0$ term of Eq. (11) into a different form. First of all, let us neglect local-field corrections. In other words, we take $\epsilon^{-1}(\mathbf{q}+0,\,\mathbf{q}+0,\,\omega)\approx\epsilon(\mathbf{q}+0,\,\mathbf{q}+0,\,\omega)^{-1}$, where $\epsilon(\mathbf{q}+0,\,\mathbf{q}+0,\,\omega)\equiv\epsilon(\mathbf{q},\omega)$ is the RPA dielectric constant defined by Eqs. (6) and (7). Substituting the expressions for $\epsilon_2(\mathbf{q},\omega)$ obtained from Eqs. (6) and (7) into the $\mathbf{K}=\mathbf{K}''=0$ term of Eq. (11), we find

$$-dE_\mathbf{p}/dt=\frac{e^4}{\pi^3}\int_{E_0<E_{\mathbf{p}-\mathbf{q}}<E_\mathbf{p}}d\mathbf{q}\int d\mathbf{k}\sum_{\mathbf{K}'}\frac{\{(E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}})|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2|\langle\mathbf{p}-\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{p}\rangle|^2 \times[f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})]\delta(E_\mathbf{p}+E_\mathbf{k}-E_{\mathbf{p}-\mathbf{q}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})\}}{q^4|\epsilon(\mathbf{q},\,E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}})|^2} \tag{29}$$

$$=\frac{e^4}{\pi^3}\sum_{\mathbf{K}'}\int_0^{E_\mathbf{p}-E_0}\alpha d\alpha\int_{E_{\mathbf{p}-\mathbf{q}}=E_\mathbf{p}-\alpha}\frac{dS_\mathbf{q}}{|\nabla_\mathbf{q}E_{\mathbf{p}-\mathbf{q}}|}\int_{E_\mathbf{k}=E_{\mathbf{k}+\mathbf{q}+\mathbf{K}''-\alpha}}dS_\mathbf{k}$$

$$\times\frac{\{|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2|\langle\mathbf{p}-\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{p}\rangle|^2[f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})]\}}{|\nabla_\mathbf{k}(E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|\,q^4|\epsilon(\mathbf{q},\,E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}})|^2}. \tag{30}$$

Equation (30) has been obtained from Eq. (29) by writing

$$d\mathbf{q}=\frac{dS_\mathbf{q}\,d(E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}})}{|\nabla_\mathbf{q}(E_{\mathbf{p}-\mathbf{q}}-E_\mathbf{p})|}$$

and by denoting $E_\mathbf{p}-E_{\mathbf{p}-\mathbf{q}}$ by $\alpha$. A further rearrangement of terms can be made, using the property of the zero-temperature Fermi distribution function that

$$f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})=f_0(E_\mathbf{k})[1-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})]-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})[1-f_0(E_\mathbf{k})].$$

Since in the integrand of Eq. (30), $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_\mathbf{k}+\alpha\geqslant E_\mathbf{k}$, the term $f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})[1-f_0(E_\mathbf{k})]$ does not contribute. We would like to explicitly carry out the integration over the variable $E_\mathbf{k}$, so as to be able to eliminate the factor $f_0(E_\mathbf{k})[1-f_0(E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})]=f_0(E_\mathbf{k})[1-f_0(E_\mathbf{k}+\alpha)]$ by incorporating it into the limits of that integration. We do this by writing

$$dS_\mathbf{k}=dk_{\parallel}dk_{\perp}=dk_{\parallel}\,|dk_{\perp}/dE_\mathbf{k}|\,dE_\mathbf{k},$$

where $dk_{\parallel}$ and $dk_{\perp}$ are elements of length in the surface $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_\mathbf{k}+\alpha$ parallel and perpendicular, respectively, to the intersection of this surface with the surface $E_\mathbf{k}=\beta$. We may thus write (denoting the product of matrix

elements by $P$):

$$\int_{E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_{\mathbf{k}}+\alpha} dS_{\mathbf{k}} \frac{Pf_0(E_{\mathbf{k}})[1-f_0(E_{\mathbf{k}}+\alpha)]}{|\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|} = \int d\beta f_0(\beta)[1-f_0(\beta+\alpha)] \int_l dk_{\parallel} \frac{|dk_\perp/dE_{\mathbf{k}}|P}{|\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|}$$

$$= \int_{E_0-\alpha}^{E_0} d\beta \int_l dk_{\parallel} \frac{|dk_\perp/dE_{\mathbf{k}}|P}{|\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|}, \quad (31)$$

$l$: intersection of $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=\alpha+\beta$ with $E_{\mathbf{k}}=\beta$. Finally, we must evaluate $|dk_\perp/dE_{\mathbf{k}}| = |dE_{\mathbf{k}}/dk_\perp|^{-1}$. Now $|dE_{\mathbf{k}}/dk_\perp| = |\nabla_{\mathbf{k}}E_{\mathbf{k}}\cdot\hat{u}|$, where $\hat{u}$ is a unit vector in the surface $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_{\mathbf{k}}+\alpha$ ($\mathbf{q}$ held fixed) normal to the line of intersection of this surface with the surface $E_{\mathbf{k}}=\beta$. Clearly

$$\hat{r}=\frac{\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})}{|\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|}$$

is a unit vector normal to the surface $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_{\mathbf{k}}+\alpha$, and

$$\hat{s}=\frac{\nabla_{\mathbf{k}}E_{\mathbf{k}}\times\nabla_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}}{|\nabla_{\mathbf{k}}E_{\mathbf{k}}\times\nabla_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|}$$

is a unit vector in the surface tangent to a line of constant $E_{\mathbf{k}}$. Hence, $\hat{u}=\hat{r}\times\hat{s}$, and we easily find that $|dE_{\mathbf{k}}/dk_\perp| = |\nabla_{\mathbf{k}}E_{\mathbf{k}}\times\nabla_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|\,|\nabla_{\mathbf{k}}(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'})|^{-1}$. Thus, we obtain finally

$$-dE_{\mathbf{p}}/dt=\frac{e^4}{\pi^3}\int_0^{E_{\mathbf{p}}-E_0}\alpha d\alpha\int_S dS_{\mathbf{q}}\frac{|\langle\mathbf{p}-\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{p}\rangle|^2}{|\nabla_{\mathbf{q}}E_{\mathbf{p}-\mathbf{q}}|q^4|\epsilon(\mathbf{q},\alpha)|^2}\sum_{\mathbf{K}}\int_{E_0-\alpha}^{E_0}d\beta\int_l dk_{\parallel}\frac{|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|}{|\nabla_{\mathbf{k}}E_{\mathbf{k}}\times\nabla_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|}, \quad (32)$$

$S$: $E_{\mathbf{p}-\mathbf{q}}=E_{\mathbf{p}}-\alpha$, $l$: intersection of $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=\alpha+\beta$ with $E_{\mathbf{k}}=\beta$.

Is is important to note that no approximations have been made in the foregoing rearrangement procedure. Now consider the case when $E_{\mathbf{p}}\approx E_0$. Then we may write

$$\int_{E_0-\alpha}^{E_0} d\beta K(\beta,\cdots)\approx\alpha K(E_0,\cdots),$$

where $K$ denotes the integrand of Eq. (32), and then set $\alpha$ equal to zero where it appears in the denominators and in the remaining limits of integration. Noting that $\epsilon_2(\mathbf{q},0)=0$, this gives

$$-dE_{\mathbf{p}}/dt=\frac{e^4}{\pi^3}\frac{(E_{\mathbf{p}}-E_0)^3}{3}\int_{S'}\frac{dS_{\mathbf{q}}|\langle\mathbf{p}-\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{p}\rangle|^2}{|\nabla_{\mathbf{q}}E_{\mathbf{p}-\mathbf{q}}|q^4\epsilon_1(\mathbf{q},0)^2}\sum_{\mathbf{K}'}\int_{l'}dk_{\parallel}\frac{|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{x}}|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2}{|\nabla_{\mathbf{k}}E_{\mathbf{k}}\times\nabla_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|}, \quad (33)$$

$S'$: $E_{\mathbf{p}-\mathbf{q}}=E_0$, $l'$: intersection of $E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_0$ with $E_{\mathbf{k}}=E_0$, a result which only involves $\nabla_{\mathbf{k}}E_{\mathbf{k}}$ and the electron wave function $\psi_{\mathbf{k}}(\mathbf{x})$ at points $\mathbf{k}$ on the Fermi surface. Equation (33) gives an explicit expression for the coefficient of $(E_{\mathbf{p}}-E_0)^3$, the leading term in a power series development of $dE_{\mathbf{p}}/dt$ around $E_{\mathbf{p}}=E_0$. The approximations made on the integrand of Eq. (32) to obtain Eq. (33) are only valid if the resulting integrals in Eq. (33) converge. If these integrals diverge, a more singular behavior of $dE_{\mathbf{p}}/dt$ at the Fermi surface than $(E_{\mathbf{p}}-E_0)^3$ is indicated.

In the case of a free electron gas,

$$|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle| = \delta_{\mathbf{K}',0}$$

and only the $\mathbf{K}'=0$ term of the sum over $\mathbf{K}'$ in Eq. (33) contributes. In the case of a real metal,

$$|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}\rangle| < 1$$

and

$$|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle| \neq 0.$$

Note that the sum of these weighting coefficients is always 1:

$$\sum_{\mathbf{K}'}|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2=1. \quad (34)$$

Not all values of $\mathbf{K}'$ can contribute: The vector $\mathbf{K}'$ contributes only if there is a point $\mathbf{k}$ on the Fermi surface and a vector $\mathbf{q}$ from the point $-\mathbf{p}$ on the Fermi surface to any other point on the Fermi surface, such that $\mathbf{k}+\mathbf{q}+\mathbf{K}'$ also lies on the Fermi surface. (In symbols, this is $E_{\mathbf{k}}=E_{-\mathbf{p}}=E_{-\mathbf{p}+\mathbf{q}}=E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}=E_0$.) This condition is satisfied only for a few of the smallest reciprocal vectors $\mathbf{K}'$; clearly a necessary, but not sufficient condition for $\mathbf{K}'$ to contribute is that $|\mathbf{K}'|\leqslant 2d$, where $d$ is the maximum diameter of the Fermi surface. Thus, if $|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2$ is appreciable for values

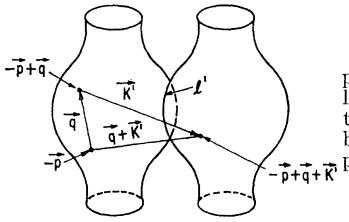


FIG. 1. Geometric interpretation of Eq. (35). The line $l'$ is the intersection of the Fermi surface, displaced by $\mathbf{q}+\mathbf{K}'$, with the undisplaced Fermi surface.

of $\mathbf{K}'$ which do *not* satisfy this condition, only part of the sum of Eq. (34) contributes. This would tend to reduce the rate of energy loss of the hot electron.

Let us now consider in detail the effect of the shape of the surface $E_\mathbf{k}$ on the hot-electron energy-loss rate. Since we are not primarily interested in effects arising from the detailed nature of the matrix elements, we replace $|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2$ by an appropriate average over $\mathbf{k}$:

$$|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2\rightarrow\langle|\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle|^2\rangle_{\mathrm{avk}}\equiv S(\mathbf{q},\mathbf{K}').$$

Denoting $|\langle\mathbf{p}-\mathbf{q}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{p}\rangle|^2$ by $|M(\mathbf{q},0)|^2$ as before, we have

$$-\frac{dE_\mathrm{p}}{dt}=\frac{e^4}{\pi^3}\frac{(E_\mathrm{p}-E_0)^3}{3}\sum_{\mathbf{K}'}J_{\mathbf{K}'},$$

$$J_{\mathbf{K}'}=\int_{S'}\frac{dS_\mathbf{q}|M(\mathbf{q},0)|^2S(\mathbf{q},\mathbf{K})}{|\nabla_\mathbf{q}E_{\mathbf{p}-\mathbf{q}}|[q^2\epsilon_1(\mathbf{q},0)]^2}\times\int_{l'}\frac{dk_{\mathrm{II}}}{|\nabla_\mathbf{k}E_\mathbf{k}\times\nabla_\mathbf{k}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|},\quad(35)$$

with $S'$ and $l'$ the same as in Eq. (33). A geometric interpretation of the line integral is simple. The surface integral is over all vectors $\mathbf{q}$ such that $-\mathbf{p}+\mathbf{q}$ lies on the Fermi surface. For each such $\mathbf{q}$, we translate the Fermi surface first by $\mathbf{q}$ and then by $\mathbf{K}'$. This translated Fermi surface either does not intersect the original Fermi surface, or intersects it, in general, in a line. Clearly $|\nabla_\mathbf{k}E_\mathbf{k}\times\nabla_\mathbf{k}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|$ is the magnitude of the cross product of the gradients of the two surfaces at a point on this line of intersection; $dk_{\mathrm{II}}$ is the element of length of this line and $\int dk_{\mathrm{II}}$ extends over the entire line of intersection. This geometrical construction is illustrated in Fig. 1. If the original and displaced Fermi surfaces are tangent along a part of the line of intersection which is of finite measure, the line integral

$$\int_{l'}\frac{dk_{\mathrm{II}}}{|\nabla_\mathbf{k}E_\mathbf{k}\times\nabla_\mathbf{k}E_{\mathbf{k}+\mathbf{q}+\mathbf{K}'}|}$$

diverges. This fact leads to a strong dependence of $J_{\mathbf{K}'}$ on the Fermi surface geometry. Note that the presence of a factor $q^4$ in the denominator of the integral $\int dS_\mathbf{q}$ leads to no divergences. According to Eq. (6), $\epsilon(\mathbf{q},0)=1-q^{-2}G(\mathbf{q},\mathbf{q},0)$, and from Eq. (7) and the fact that $\langle\mathbf{k}|\exp(-i\mathbf{q}\cdot\mathbf{x})|\mathbf{k}+\mathbf{q}+\mathbf{K}'\rangle$ approaches $\delta_{\mathbf{K}',0}$ as $\mathbf{q}$ approaches zero,

$$\lim_{\mathbf{q}\rightarrow0}G(\mathbf{q},\mathbf{q},0)=\lim_{\mathbf{q}\rightarrow0}\frac{e^2}{\pi^2}\int d\mathbf{k}\frac{f_0(E_\mathbf{k})-f_0(E_{\mathbf{k}+\mathbf{q}})}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}}=-\frac{e^2}{\pi^2}\int_{E_\mathbf{k}=E_0}\frac{dS_\mathbf{k}}{|\nabla_\mathbf{k}E_\mathbf{k}|}\equiv-k_s^2.\quad(36)$$

Equation (36) may be taken to define $k_s$ for a nonspherical Fermi surface. Thus, as $\mathbf{q}$ approaches zero, $q^2\epsilon_1(\mathbf{q},0)$ approaches $k_s^2$. To emphasize this we will take $\epsilon_1(\mathbf{q},0)\approx1+k_s^2/q^2$ throughout the following calculations.

Let us now consider specific Fermi surface models. We will evaluate in detail only $J_0$; treatment of $J_{\mathbf{K}'}$, $\mathbf{K}'\neq0$, would be similar. First consider a spherical Fermi surface, $E_\mathbf{k}=k^2/2m$. Let us define $L(\mathbf{q})$ by

$$L(\mathbf{q})=\int_{l'}\frac{dk_{\mathrm{II}}}{|\nabla_\mathbf{k}E_\mathbf{k}\times\nabla_\mathbf{k}E_{\mathbf{k}+\mathbf{q}}|};$$

$l'$: intersection of $E_\mathbf{k}=E_0$ with $E_{\mathbf{k}+\mathbf{q}}=E_0$. Then it is easy to show that for spherical energy surfaces $L(\mathbf{q})=2\pi m^2/q$. The infinity at $\mathbf{q}=0$ results from the fact that as $\mathbf{q}$ approaches 0 the spheres approach tangency along their entire circle of intersection. Taking the matrix elements $M$ and $S$ in Eq. (35) to be unity, we find

$$J_0=\int_{E_{\mathbf{p}-\mathbf{q}}=E_0}\frac{dS_\mathbf{q}}{|\nabla_\mathbf{q}E_{\mathbf{p}-\mathbf{q}}|}\frac{2\pi m^2}{(q^2+k_s^2)^2}\frac{1}{q}=\frac{2\pi^2m^3}{k_0k_s^3}\left(\frac{2k_0k_s}{k_s^2+4k_0^2}+\tan^{-1}\frac{2k_0}{k_s}\right),\quad(37)$$

where the $\mathbf{q}$ integration is easily performed in spherical coordinates with the $z$ axis along $\mathbf{p}$. Multiplying by the factor $(E_\mathrm{p}-E_0)^3e^4/(3\pi^3)$ yields a result agreeing with the free-electron gas formula of Quinn.

The isotropy of hot-electron attenuation shown by a free-electron gas disappears when the Fermi surface is anisotropic. This can be seen explicitly by considering a Fermi surface which is an ellipsoid of revolution, $E_\mathbf{k}=k_z^2/2m_z+(k_x^2+k_y^2)/2m$, and taking $\mathbf{p}$ to make an angle $\chi$ with the $k_z$ axis. One finds that $L(\mathbf{q})=2\pi m^2m_z\times[m^2q_z^2+mm_z(q_x^2+q_y^2)]^{-1/2}$, giving the following result for $J_0$ (again taking $M=S=1$):

$$J_0=\tfrac{1}{2}\pi a^2b^4E_0^{-3}\int_0^1du\int_0^{2\pi}d\phi\,[E+2F\sin\phi+G\sin^2\phi]^{-2},$$
$$a=(2m_zE_0)^{1/2},\quad b=(2mE_0)^{1/2},$$
$$E=k_s^2+4b^2u^2+4(a^2-b^2)\cos^2\chi u^4,$$
$$F=4u^3(1-u^2)^{1/2}(a^2-b^2)\sin\chi\cos\chi,\quad(38)$$
$$G=4u^2(1-u^2)(a^2-b^2)\sin^2\chi.$$

The forms of $E$, $F$, and $G$ clearly show that $J$ depends on the orientation of $\mathbf{p}$. The $\phi$ integration can be evaluated explicitly, but the remaining integration over $u$ cannot be integrated in elementary functions, for general $\chi$.

Radically different behavior from the spherical case is found when we consider a cylindrical Fermi surface of finite length, $E_k=(k_x^2+k_y^2)/2m$ for $-L\leqslant k_z\leqslant L$. Such a Fermi surface could in principal occur in a solid, the two "open" ends touching opposite Brillouin zone faces. Using cylindrical coordinates and writing $q_r$ and $q_z$, respectively, for the radial and axial components of $\mathbf{q}$, we find

$$L(\mathbf{q})=\frac{2m^2(2L-|q_z|)}{q_r[k_0^2-q_r^2/4]^{1/2}}. \tag{39}$$

Substituting this into Eq. (35) for $J_0$ (taking the matrix elements as unity for simplicity), setting $\mathbf{p}-\mathbf{q}=\mathbf{t}'=(k_0\cos\phi, k_0\sin\phi, t')$ and $\mathbf{p}=(k_0,0,l)$ gives

$$J_0=\frac{2m^3}{k_0^2}\int_0^{2\pi}d\phi\int_{-L}^{L}dt'\frac{2L-|l-t'|}{|\sin\phi|[k_s^2+2k_0^2(1-\cos\phi)+(l-t')^2]^2}=\infty. \tag{40}$$

The reason for the divergence is clearly the fact that for all displacements $\mathbf{q}$ for which $q_r=0$ (axial displacements), the displaced and original Fermi surfaces are tangent along their intersection, making $L(\mathbf{q})$ infinite. Whereas $L(\mathbf{q})=\infty$ at isolated points $\mathbf{q}$ does not necessarily make $J_0$ diverge, $L(\mathbf{q})=\infty$ along a line (a one-dimensional continuum) in $\mathbf{q}$ does. In order to obtain an expression for the rate of energy loss, we must return to Eq. (32), using which we can obtain an explicit expression for the leading term in $dE_p/dt$ when $E_p\approx E_0$. The evaluation is complicated and we only give the result:

$$-\frac{dE_p}{dt}=\frac{2e^4}{\pi^3}\frac{m^3}{k_0^2}\left\{\int_{-L}^{L}dl'(2L-|l-t'|)\left(\frac{1}{[(l-t')^2+k_s^2]^2}+\frac{1}{3}\frac{1}{[(l-t')^2+k_s^2+4k_0^2]^2}\right)\right\}(E_p-E_0)^3$$
$$\times\left|\ln\left(\frac{E_p-E_0}{E_0}\right)\right|+O[(E_p-E_0)^3]. \tag{41}$$

We see that $dE_p/dt\propto(E_p-E_0)^3|\ln[(E_p-E_0)/E_0]|$, which explains why we get an infinite answer when we attempt to compute the coefficient of $(E_p-E_0)^3$. Clearly a material with a cylindrical Fermi surface would exhibit a much greater hot-electron absorption than would be expected on the basis of a free-electron gas model.

Since a cylindrical Fermi surface model is a very unrealistic one, it is important to look for more general conditions under which the coefficient of $(E_p-E_0)^3$ diverges. One such condition may be expressed as follows:

(i) Suppose the Fermi surface contains a straight-line segment of finite length, and that the normals to the Fermi surface along this straight line are all coplanar. Then $dE_p/dt$ is more singular than $(E_p-E_0)^3$ for all $\mathbf{p}$ on the line segment.

This is easy to see. For $\mathbf{p}$ on the straight line segment, the values taken by $\mathbf{q}$ include translation of the Fermi surface along the line segment. For these special values of $\mathbf{q}$, the displaced Fermi surface and the original Fermi surface are tangent along a finite portion of their line of intersection (that is, along the overlap of the displaced and the original line segment). Hence, for all these values of $\mathbf{q}$, $L(\mathbf{q})$ is infinite, making $J_0$ infinite. A useful special case of (i) is:

(ii) Suppose the Fermi surface contains a straight-line segment of finite length, and that a plane containing this line is a plane of reflection symmetry of the energy surfaces. Then for $\mathbf{p}$ on the line segment $dE_p/dt$ is more singular than $(E_p-E_0)^3$. This result follows from (i) by noting that, if the line is contained in a plane of reflection symmetry, the normals to the line all must lie in this plane and, hence, are coplanar. A direct, analytic proof of (ii) is presented in Appendix III.

Note that while the conditions (i) and (ii) suffice to make $J_0$ infinite, they do *not* in general suffice to make $J_K$, $\mathbf{K}\neq 0$ infinite. Thus, a statement analogous to (i) for $J_K$ would require either: (iii) that the straight line segment of (i) should be parallel to $\mathbf{K}$ and longer than $|\mathbf{K}|$, or (iv) that there should be two parallel straight line segments in the Fermi surface, one translated by $\mathbf{K}$ from the other, with the normals to the Fermi surface along the two-line segments lying in two parallel planes. These conditions are more restrictive than those of (i) and are, therefore, less likely to be approximately realized in a real metal.

We infer from (i) a general qualitative result: Flattening of the Fermi surface tends to increase the hot-electron absorption. Recent band calculations[16] and hot-electron experiments[1] on copper suggest a possible confirmation of this rule. The Fermi surface of Cu is greatly flattened in certain regions. This is illustrated in Fig. 2, obtained from the band calculation of Segall,[16] which shows the intersection of the reflection plane (110) with the Fermi surface. Clearly, much of this line of intersection is very nearly linear, and hence the conditions of (ii) are approximately satisfied. One would,

[16] B. Segall, Phys. Rev. **125**, 109 (1962).

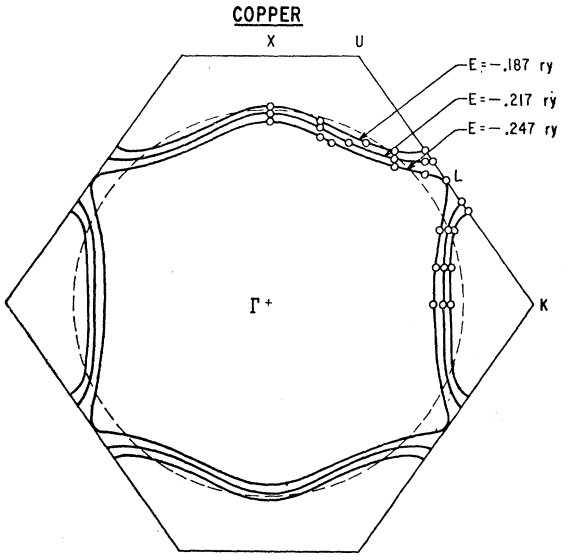


FIG. 2. Intersection of a (110) plane with the surfaces of constant energy for Cu. The estimated Fermi energy is $-0.183\pm0.010$ Ry. The dashed curve is the intersection with the free-electron sphere. Note the flatness of the Fermi surface as compared with the free-electron sphere.

thus, except an unusually large hot-electron energy-loss rate in Cu for hot electrons near the flat region of the Fermi surface. Recent photoemission experiments[1] on Cu indicate an anomalously short hot-electron range. It is possible that these results, rather than being due to oxidation of the Cu surface, as suggested by Crowell *et al.*,[1] may be attributed to unusually large hot electron attenuation produced by flattening of the Fermi surface. Further experiments on copper, with special efforts to guard against contamination of the surface, would be of interest, as would be numerical calculation of $J_0$ using available information[16,17] on the energy surfaces in Cu.

It is worth pointing out that the effects of flattening of the Fermi surface on hot electron attenuation and on the anomalous skin effect[18] are very similar: the flatter the Fermi surface, the greater the hot-electron attenuation and the greater the anomalous skin effect. Thus, there should be a rough correlation between the sizes of these two effects in different metals. Copper shows a very large anomalous skin effect,[17] so the anomalously large hot-electron attenuation in Cu found by Crowell *et al.*,[1] if correct, would provide an example of this correlation. The similarity also suggests that it might be possible to use hot-electron attenuation as a tool for studying Fermi surface properties, via Eq. (33), much as the anomalous skin effect is used for this purpose.[18] However, complications introduced by the electron-phonon interaction,[6] by umklapp and local-field effects discussed above, by many-body corrections to the RPA and by uncertainties in the $\mathbf{p}$ to be used in Eq. (33) arising from direction changes in scattering and from crystallite structure of samples, might make such an application of hot-electron range experiments unfeasible. Further investigation of this question would be worthwhile.

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## APPENDIX I

We give here the one-OPW wave functions for valence electrons in Al and outline the procedure used to obtain from them the estimates of the matrix elements quoted in the text. Letting $N$ denote the number of unit cells in the crystal, $V_a$ the unit cell volume and $\mathbf{R}_\nu$ a lattice translation vector, we may write the one-OPW wave function $\psi_{\mathbf{k}}(\mathbf{x})$ as[7]

$$\psi_{\mathbf{k}}(\mathbf{x})=(NV_a)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{x}) -N^{-1/2}\sum_\nu\sum_{n,l}\exp(i\mathbf{k}\cdot\mathbf{R}_\nu)A_{nl}(\mathbf{k})u_{nl;\mathbf{k}}(\mathbf{x}-\mathbf{R}_\nu).$$

The atomic wave function $u_{nl;\mathbf{k}}$ is given by

$$u_{nl;\mathbf{k}}(\mathbf{x})=x^{-1}P_{nl}(x)Y_{l0}(\mathbf{x}\cdot\mathbf{k}_u),$$

where $P_{nl}$ is the radial part, $Y_{l0}$ is a spherical harmonic, and $\mathbf{k}_u$ is a unit vector in the $\mathbf{k}$ direction. The core orthogonalization coefficient $A_{nl}(\mathbf{k})$ is given by[7]

$$A_{nl}(\mathbf{k})=[4\pi(2l+1)V_a^{-1}]^{1/2}i^l\int_0^\infty dx\, xP_{nl}(x)j_l(kx).$$

Evaluation of $\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle$ using this wave function leads to the result

$$\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle N_{\mathbf{p}}N_{\mathbf{p}-\mathbf{q}}$$
$$=\delta_{\mathbf{K},0}-S(\mathbf{K})\Big\{\sum_{nl}A_{nl}^*(\mathbf{p}-\mathbf{q})A_{nl}(\mathbf{p}-\mathbf{q}-\mathbf{K})P_l[(\mathbf{p}-\mathbf{q})_u\cdot(\mathbf{p}-\mathbf{q}-\mathbf{K})_u]$$
$$+\sum_{nl}A_{nl}(\mathbf{p})A_{nl}^*(\mathbf{p}+\mathbf{K})P_l[\mathbf{p}_u\cdot(\mathbf{p}+\mathbf{K})_u]-\sum_{nl}\sum_{n'l'}A_{nl}(\mathbf{p})A_{n'l'}^*(\mathbf{p}-\mathbf{q})$$
$$\times\int d\mathbf{x}\, u^*_{n'l';\mathbf{p}-\mathbf{q}}(\mathbf{x})\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]u_{l\,\mathbf{p}}(\mathbf{x})\Big\}. \quad \text{(A1)}$$

[17] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A250**, 325 (1957).
[18] A. B. Pippard, Proc. Roy. Soc. (London) **A224**, 273 (1954).

Here $S(\mathbf{K})$ is the crystallographic structure factor, $P_l$ is the $l$th Legendre polynomial, and the normalization factors are defined by $N_p^2=1-S(0)\sum_{nl}|A_{nl}(\mathbf{p})|^2$.

In calculating the orthogonalization coefficients in Al, orthogonalized Slater radial orbitals[19] are used (in the following equations, $a_0$ is the radius of the first Bohr orbit in hydrogen):

$$P_{1s}=Ar\exp(-\lambda_1 r),\quad P_{2s}=Cr^2\exp(-\lambda_2 r)-Dr\exp(-\lambda_1 r),\quad P_{2p}=Br^2\exp(-\lambda_2 r);$$

$$A=2\lambda_1^{3/2},\quad B=(2/\sqrt{3})\lambda_2^{5/2},\quad C=B(1-\alpha^2)^{-1/2},\quad D=A\alpha(1-\alpha^2)^{-1/2};$$

$$\alpha=\frac{24}{\sqrt{3}}\frac{\lambda_2^{5/2}\lambda_1^{3/2}}{(\lambda_1+\lambda_2)^4};\quad \lambda_1=\frac{12.7}{a_0},\quad \lambda_2=\frac{4.4}{a_0}.$$

These radial orbitals lead to

$$A_{1s}(\mathbf{k})=\left(\frac{4\pi}{V_a}\right)^{1/2}\frac{2A\lambda_1}{(\lambda_1^2+k^2)^2},\quad A_{2s}(\mathbf{k})=2\left(\frac{4\pi}{V_a}\right)^{1/2}\left[\frac{C(3\lambda_2^2-k^2)}{(\lambda_2^2+k^2)^3}-\frac{D\lambda_1}{(\lambda_1^2+k^2)^2}\right],$$

$$A_{2p}(\mathbf{k})=i\left(\frac{12\pi}{V_a}\right)^{1/2}\frac{8kB\lambda_2}{(\lambda_2^2+k^2)^3}.$$

Using these expressions, we obtain an explicit form for the $1s$ orbital contribution to Eq. (A1):

$$\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle_{1s}N_pN_{p-q}=\delta_{K,0}-\frac{4\pi}{V_a}16\lambda_1^5S(\mathbf{K})\{[\lambda_1^2+|\mathbf{p}-\mathbf{q}|^2]^{-2}[\lambda_1^2+|\mathbf{p}-\mathbf{q}-\mathbf{K}|^2]^{-2}$$
$$+[\lambda_1^2+|\mathbf{p}|^2]^{-2}[\lambda_1^2+|\mathbf{p}+\mathbf{K}|^2]^{-2}-16\lambda_1^4[4\lambda_1^2+|\mathbf{q}+\mathbf{K}|^2]^{-2}[\lambda_1^2+|\mathbf{p}|^2]^{-2}[\lambda_1^2+|\mathbf{p}-\mathbf{q}|^2]^{-2}\}. \quad \text{(A2)}$$

Now let us use Eqs. (A1) and (A2) to estimate the matrix elements. In Eq. (A2), we notice that for $\mathbf{q}$, $\mathbf{K}$, and $\mathbf{p}-\mathbf{q}$ small compared to $\lambda_1$, the three terms in the curly bracket are nearly equal, and so the negative part cancels half of the positive part. We assume that this is approximately true for Eq. (A1), i.e., that

$$\langle\mathbf{p}-\mathbf{q}|\exp[-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{x}]|\mathbf{p}\rangle N_pN_{p-q}\approx\delta_{K,0}-\tfrac{1}{2}S(\mathbf{K})\{\textstyle\sum_{nl}A_{nl}^*(\mathbf{p}-\mathbf{q})A_{nl}(\mathbf{p}-\mathbf{q}-\mathbf{K})P_l[(\mathbf{p}-\mathbf{q})_u\cdot(\mathbf{p}-\mathbf{q}-\mathbf{K})_u]$$
$$+\textstyle\sum_{nl}A_{nl}(\mathbf{p})A_{nl}^*(\mathbf{p}+\mathbf{K})P_l[\mathbf{p}_u\cdot(\mathbf{p}+\mathbf{K})_u]\}. \quad \text{(A3)}$$

Equations (A2) and (A3) are now used to calculate, for small $\mathbf{q}$, $\mathbf{K}$, and $\mathbf{p}-\mathbf{q}$, numerical estimates of the averages of the squared matrix elements over the directions of $\mathbf{p}$ and $\mathbf{p}-\mathbf{q}$. Using $A_{1s}(k_0)\approx0.149$, $A_{2s}(k_0)\approx0.084$, $A_{2p}(k_0)\approx0.068$, we find that

$$\begin{aligned}&\langle|M(\mathbf{q},\mathbf{K})|^2\rangle_{av}\approx0.02,\\ &\langle|M_s(\mathbf{q},\mathbf{K})|^2\rangle_{av}\approx0.008\approx0.01,\end{aligned} \quad \text{(A4)}$$

where $M(\mathbf{q},\mathbf{K})$ is the entire matrix element, Eq. (A3), and $M_s(\mathbf{q},\mathbf{K})$ is the $1s$ orbital contribution, Eq. (A2). In the numerical estimate of the contribution of umklapp processes to the plasmon creation rate quoted in the text, the value of the matrix element $|M_s|^2$ given in (A4) was multiplied by $\frac{1}{2}$, a correction for the decrease of $M_s$ with increasing $\mathbf{K}$.

From Eq. (A2) we see that $M_s(\mathbf{q},\mathbf{K})$ is negative for small $\mathbf{K}$, but then becomes positive as $\mathbf{K}$ increases, since the first two terms in the curly bracket decrease faster with increasing $\mathbf{K}$ than does the third term. Thus, neglecting $\mathbf{p}$ and $\mathbf{q}$ in comparison with $\mathbf{K}$, we find that $M_s(\mathbf{K})<0$ for $|\mathbf{K}|<0.8\lambda_1$, and $M_s(\mathbf{K})>0$ for $|\mathbf{K}|>0.8\lambda_1$. Qualitatively similar behavior is expected for the full matrix element $M$. This behavior is the reason for the choice of the $1s$ and $2s$, $p$ cutoffs as smaller than $0.8\lambda_1$, and $0.8\lambda_2$, respectively.

[19] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1958), p. 163.

## APPENDIX II

We state here some properties of the free-electron gas. The RPA dielectric constant for the free-electron gas was first calculated by Lindhard.[20] It is given by

$$\epsilon_F=\epsilon_{F1}+i\epsilon_{F2},$$
$$\epsilon_{F1}(\mathbf{q},\omega)=1+\frac{3\omega_p^2}{q^2v_0^2}\left\{\frac{1}{2}+\frac{1}{8z}[1-(z-\mu)^2]\ln\left(\frac{z-\mu+1}{z-\mu-1}\right)\right.$$
$$\left.+\frac{1}{8z}[1-(z+\mu)^2]\ln\left(\frac{z+\mu+1}{z+\mu-1}\right)\right\}, \quad \text{(A5)}$$
$$\epsilon_{F2}(\mathbf{q},\omega)=\frac{3\omega_p^2}{q^2v_0^2}$$
$$\times\begin{cases}\frac{1}{2}\pi\mu, & z+\mu<1\\ (\pi/8z)[1-(z-\mu)^2], & |z-\mu|<1<z+\mu\\ 0, & |z-\mu|>1\end{cases}$$

where $z=q/2k_0$ and $\mu=\omega/qv_0$.

[20] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, No. 8 (1954).

The rate of energy loss for a hot electron of $E \approx E_0$ in a free-electron gas is[4]

$$F = -\frac{dE_p}{dt} = \frac{2m^3e^4}{3\pi k_0 k_s^3}\left[\frac{2k_0k_s}{k_s^2+4k_0^2} + \tan^{-1}\frac{2k_0}{k_s}\right](E_p - E_0)^3. \tag{A6}$$

The rate of energy loss due to plasmon creation in a free-electron gas, in the notation employed in the text, is[4]

$$F' = -\frac{dE_p}{dt} = \frac{me^2\omega_p^2}{p}\ln\frac{\nu - k_0}{p-\mu}. \tag{A7}$$

## APPENDIX III

We give here an analytic proof of the assertion (ii): Suppose the Fermi surface contains a straight line segment of finite length, and that a plane containing this line is a plane of reflection symmetry of the energy surfaces. Then for $\mathbf{p}$ on the line, $dE_p/dt$ is more singular than $(E_p - E_0)^3$.

Proof: Let us take the straight line segment to be along the $z$ axis of our coordinate system, with the origin at $\mathbf{p}$, which is assumed to lie on the line segment. Let the energy surfaces be symmetric under the reflection $x \to -x$. Then we clearly may write

$$E = E_0 + yF(z) + y^2G(x^2,y,z) + x^2R(x^2,y,z).$$

We assume all the functions appearing here to be analytic in a neighborhood of $x=y=0$. The condition $E=E_0$ defines a surface $y=\Lambda(x,z)$; by hypothesis $\Lambda(0,z)=0$. Consider now the two possible cases:

Case I: $R(x^2,0,z) \neq 0$.

This implies that $R(x^2,0,z) \approx x^{N-2}r(z) + O(x^N)$ with $N$ even, $N \geqslant 2$ and $r(z)$ finite. Thus $\Lambda(x,z) = x^N H(x^2,y,z)$ with finite $H(0,0,z)$.

Case II: $R(x^2,0,z) = 0$.

This implies $R(x^2,y,z) = yQ(x^2,y,z)$, so that $E$ equals $E_0$ on a strip of the $xz$ plane, making $J_0$ clearly singular. Let us restrict ourselves to the nontrivial Case I. We may write $E = E_0 + [y - x^N H(x^2,y,z)]B(x^2,y,z)$, where the function $B$ is well behaved for small $x$ and $y$. We wish to calculate a lower bound for the integral $J_0$, which we recall is given by (taking matrix elements as unity for simplicity)

$$J_0 = \int_{S'} \frac{dS_q}{|\nabla_q E_{p-q}|\, q^4 \epsilon_1(\mathbf{q},0)^2} \int_{l'} \frac{dk_{\parallel}}{|\nabla_k E_k \times \nabla_k E_{k+q}|},$$

$S'$: $E_{p-q} = E_0$, $l'$: intersection of $E_k = E_0$ with $E_{k+q} = E_0$. Clearly,

$$\begin{aligned} E_q = E_0 \quad &\text{implies} \quad q_y = q_x^N H(q_x^2, q_y, q_z); \\ E_k = E_0 \quad &\text{implies} \quad k_y = k_x^N H(k_x^2, k_y, k_z); \\ E_{k+q} = E_0 \quad &\text{implies} \quad k_y + q_y = (k_x+q_x)^N \\ &\qquad \times H[(k_x+q_x)^2, k_y+q_y, k_z+q_z]. \end{aligned}$$

Combining these equations gives

$$\begin{aligned} k_x^N H(k_x^2,k_y,k_z) + q_x^N H(q_x^2,q_y,q_z) \\ = (k_x+q_x)^N H[(k_x+q_x)^2, k_y+q_y, k_z+q_z] \end{aligned}$$

which for $q_x \neq 0$ implies that

$$k_x = \alpha(\mathbf{k},\mathbf{q}) q_x$$

with $\alpha((0,0,k_z),(0,0,q_z))$ finite. Now it is easy to calculate that

$$\begin{aligned} \nabla_k E_k|_f &= B(\mathbf{k})[-Nq_x^{N-1}H(\mathbf{k})\alpha^{N-1}, 1, 0] \\ &\quad - q_x^N \alpha^N B(\mathbf{k}) \nabla_k H(\mathbf{k}), \\ \nabla_k E_{k+q}|_f &= B(\mathbf{k}+\mathbf{q})[-Nq_x^{N-1}H(\mathbf{k}+\mathbf{q})(\alpha+1)^{N-1}, 1, 0] \\ &\quad - q_x^N(\alpha+1)^N B(\mathbf{k}+\mathbf{q}) \nabla_k H(\mathbf{k}+\mathbf{q}), \end{aligned}$$

where the subscript $f$ means that the derivatives have been evaluated on the Fermi surface. Thus, for $E_k = E_{k+q} = E_0$ we have

$$\begin{aligned} |\nabla_k E_k \times \nabla_k E_{k+q}| &\leqslant |B(\mathbf{k})B(\mathbf{k}+\mathbf{q})| \\ &\quad \times N[|H(\mathbf{k})||\alpha|^{N-1} + |H(\mathbf{k}+\mathbf{q})||\alpha+1|^{N-1}] q_x^{N-1} \\ &\quad + O(q_x^N) \equiv q_x^{N-1}\gamma(\mathbf{k},\mathbf{q}), \end{aligned}$$

with $\gamma$ finite. Writing $\int dS_q = \int dq_x dq_z |\sec \mathbf{n}_u(\mathbf{q}) \cdot \mathbf{y}_u|$, where $\mathbf{n}_u(\mathbf{q})$ and $\mathbf{y}_u$ are unit vectors, we have

$$J_0 \geqslant \int_{S'} \frac{|\sec \mathbf{n}_u(\mathbf{q}) \cdot \mathbf{y}_u|}{|\nabla_q E_{p-q}|\, q^4 \epsilon_1(\mathbf{q},0)^2} \frac{dq_x dq_z}{q_x^{N-1}} \int_{l'} \frac{dk_{\parallel}}{\gamma(\mathbf{k},\mathbf{q})}, \tag{A8}$$

which clearly diverges, since $N \geqslant 2$. Thus, $J_0$ is singular, and $dE_p/dt$ is more singular than $(E_p - E_0)^3$.