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Brief Reports

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Slow electrons in condensed matter

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The irreversible thermalization of energy lost by an electron in amorphous condensed matter makes successive losses incoherent. This allows us to extend a stochastic treatment of electron degradation down to the thermal range. The probability of a given momentum and energy transfer is viewed as a macroscopic property of each material, which reduces to the structure factor $S(\mathbf{q},\omega)$ in the Born approximation. The identification of such bulk properties presents novel challenges for experimentalists.

Electrons are a main agent for the distribution of the energy of ionizing radiations. The processes of penetration, degradation, and diffusion of these radiations have been analyzed quantitatively, mainly in the 1950s.[1-3] However, those studies failed to reach the terminal stage of electron action on condensed matter, namely, the *subexcitation* range[4] of energies below the ionization threshold, inaccessible to experiment or theory at that time. Subexcitation electrons actually deal out an appreciable fraction of the total energy (~10–20%) and of its chemical action, e.g., by disturbing molecular equilibria and by forming negatively charged complexes.

Recent developments in electron spectrometry and in the preparation of ultrathin (~1 nm) samples, now permit quantitative observations of slow electrons. Substantial efforts have been devoted to these studies by Sanche and Michaud[5] and by others. Developments of comparable novelty on the theory side are now in order.

Recall that fast electrons deal out energy through localized elementary processes separated by free paths larger than atomic dimensions. Their degradation is accordingly treated stochastically. Slow electrons are instead delocalized, since their wavelength exceeds the atomic size, and have short free paths on the order of 1 nm. They should then be dealt with in a quantum frame rather than by classical models.

This paper argues that the stochastic treatment of electron energy degradation remains, in fact, appropriate in a quantum mechanical context, regardless of the restriction on the localization of each loss process inherent in the long wavelength of slow electrons. After documenting this starting point, we shall outline how the treatment of subexcitation electrons may be developed in this novel context.

To this end, we shall introduce the theory and classification of diverse, specific processes of energy loss drawing attention to relevant properties of each material, some of which are partially known, others still poorly identified. We may thus provide guidance for experiments on the direct study of slow electrons as well as on material properties relevant to this study.

The formulation of a stochastic treatment of electron energy degradation hinges on identifying a sequence of distinct elementary energy transfers from an electron to its environment. This identification is trivial in the environment of a molecular gas where each energy transfer results from a collision that imparts an observable recoil and a definite rovibrational excitation, or anyhow when the transfers are well separated in space.[1] In condensed phases, on the other hand, a slow electron keeps interacting with matter after each energy loss. Rather it is the transferred energy that becomes separated from the electron, not necessarily in space but mainly by percolating from one degree of freedom to another as it gets thermalized. The separation becomes irreversible as the likelihood of the energy coherently reacting back on the electron becomes negligible; we thus view incoherence as resulting from "irreversible thermalization." The dissipation process manifests itself physically by setting a lower limit to the sharpness of condensed matter spectra as compared to spectra in gas phases; this limit provides an index of the relaxation time of excitation in condensed matter. The dissipation manifests itself formally in the operation of summing over the excitation probabilities of the multitude of final channels accessible in condensed matter. This operation formalizes the incoherence of successive energy transfers.

On this basis we introduce as a stochastic element the probability of an elementary transfer event per unit path length of a subexcitation electron of energy ε. This probability, $k_\varepsilon(\mathbf{q},\omega)$, is differential in the energy transfer $\hbar\omega$ and momentum transfer $\hbar\mathbf{q}$; the momentum transfer $\hbar\mathbf{q}$ contributes to the angular diffusion of the electron. The parameter k_ε represents the net effect of the electron's Coulomb interaction with all the surrounding nuclei and electrons within a volume of size at least comparable to the electron wavelength. We regard k_ε as a semimacroscopic property of matter to be determined by experiment or theory without relying on its microscopic analysis.

Fragmentary evidence on the contribution to $k_\varepsilon(\mathbf{q},\omega)$ by specific processes is available from various studies, dealing mostly with thermal or epithermal values of ε. Evidence on the comparative roles of larger and lower values of ω in the degradation process might be gleaned from electron energy spectra following transmission or backscattering from films.[5] A comprehensive analysis of the contributions to k_ε by diverse processes is deferred to separate reports. Here we note that studies on the motion of slow electrons in condensed phases of rare and diatomic gases have demonstrated multiple minima in the transmission spectra for electron energies corresponding to band gaps of microcrystalline structures.[6] Our paper concerns amorphous matter primarily; it also applies to crystalline matter insofar as the mean-free path remains much smaller than inhomogeneities and sample size. Accordingly, we do not rely explicitly on the usual concepts of band theory, and on the related analysis of degradation parameters.[7] However, the zero point of the scale of ε may take into account an average interaction between electron and medium, and the dispersion relation $\varepsilon = \hbar^2 p^2/2m$ may involve an effective mass.

The state of a subexcitation electron subject to random-loss processes is represented by a density matrix $(\mathbf{r}'|\rho|\mathbf{r}'')$ or by its Fourier transformation in $\mathbf{r}'-\mathbf{r}''$, $N(\mathbf{r},\mathbf{p})$— the Wigner distribution function—where $\mathbf{r}=\frac{1}{2}(\mathbf{r}'+\mathbf{r}'')$ and $\hbar\mathbf{p}$ plays the role of the electron's momentum.[8] The electron flux measured by a detector of unit area orthogonal to $\mathbf{p}$ at the point $\mathbf{r}$ is related (but not equal) to $(p/m)N(\mathbf{r},\mathbf{p})$. The function $N(\mathbf{r},\mathbf{p})$ for electrons in a macroscopically homogeneous and isotropic material obeys a Boltzmann-type equation with kernel $k_\varepsilon(\mathbf{q},\omega)$ [Eq. (1) following].

Direct approach to the calculation of $k_\varepsilon(\mathbf{q},\omega)$ by solution of the electron's Schrödinger equation in the field of each material of interest appears unpromising. The alternative considered here is to seek expressions of k_ε in terms of material properties that are—or could be—accessible by various techniques aimed at testing the material's ability to absorb quanta of momentum and energy. First among such properties is the *structure factor* $S(\mathbf{q},\omega)$[9] accessible primarily by x-ray and neutron diffraction. Both of these probes interact weakly with electrons and nuclei, respectively, thus studying complementary aspects of matter's ability to absorb momentum and energy. An exploratory study has, in fact, demonstrated an experimental correlation between the electron mobilities and x-ray stucture factors of pentane isomers.[10] Indeed, the Born approximation to $k_\varepsilon(\mathbf{q},\omega)$ is proportional to $S(\mathbf{q},\omega)$, although it holds mainly for small values of $\mathbf{q}(\ll 1\ \mathrm{nm}^{-1})$. Other analytical probes, such as magnetic resonance, provide further complementary information on $S(\mathbf{q},\omega)$. A complete mapping of S on the $(\mathbf{q},\omega)$ surface for a specific material remains today a feasible but nontrivial task.

The values of $S(\mathbf{q},\omega)$ at low q values represent bulk properties of a material, typically the excitation of acoustic plane waves which are also responsible for the Brillouin scattering of light. The contribution of acoustic excitations to the dissipation of electron energy is restricted by the weakness of the interaction and by conservation of energy and momentum, but remains to be studied extensively. Excitation of optically active modes—accessible to infrared spectroscopy—should yield an even greater contribution. Density fluctuations of matter other than plane waves also contribute to electron diffusion and slowing down. Evaluation of slow electron coupling to density fluctuations of matter in terms of atomic parameters has been introduced by Cohen and co-workers[11] in the context of electron mobility in liquid argon. The same approach may prove effective in the larger context of the present paper.

The q dependence of $S(\mathbf{q},\omega)$ in the range $1 \le q \le 10$ nm^{-1}, is presumably most relevant to the motion and degradation of subexcitation electrons. Here the Born approximation is generally inadequate, as incoherent energy and momentum transfers result generally from the coherent superposition of manifold *virtual* transfers. Thus originates typically the resonant formation of temporary negative-ion complexes which contribute heavily to electron degradation.[12] Processes in this range are central to the determination of the probability $k_\varepsilon(\mathbf{q},\omega)$ of an incoherent momentum and energy transfer by an electron of energy ε, a subject we shall return to below.

Knowledge of $k_\varepsilon(\mathbf{q},\omega)$ will enable one to study the steady-state distribution $N(\mathbf{r},\mathbf{p})$ generated by a constant source, through the procedure of Ref. 3. The procedure unravels the calculation of N into a sequence of steps beginning with a Boltzmann equation integrated over $\mathbf{r}$ and over the direction of $\mathbf{p}$:

(a) The integral $\int d\mathbf{r}\, d\hat{\mathbf{p}}\, N(\mathbf{r},\mathbf{p})$ represents the basic *spectral distribution* $N(\varepsilon)$ of the subexcitation electrons. Regardless of the classical or quantum interpretation of $N(\mathbf{r},\mathbf{p})$,[8] its integral $N(\varepsilon)$ is determined by the equilibrium between the removal of electrons of energy ε through all energy transfers and the additions to $N(\varepsilon)$ by transfers from $N(\varepsilon+\hbar\omega)$ or by an isotropic source $S(\varepsilon)$ of electrons of that energy. There results the equations

$$\begin{aligned} \mu(\varepsilon)N(\varepsilon) &= \int d\omega\, N(\varepsilon+\hbar\omega) \int d\mathbf{q}\, k_{\varepsilon+\hbar\omega}(\mathbf{q},\omega) + S(\varepsilon)\,, \\ \mu(\varepsilon) &= \int d\omega \int d\mathbf{q}\, k_\varepsilon(\mathbf{q},\omega)\,, \end{aligned} \tag{1}$$

readily amenable to numerical solutions which have been studied extensively for faster electrons.[1,3] The spectrum of ω actually extends to negative frequencies of order $\sim -kT$, because of interaction with thermal motions of the medium. Allowing for this effect will require modification of the procedure of Ref. 3 which was designed for Volterra-type equations.

(b) The next step deals with the integral of $N(\mathbf{r},\mathbf{p})$ weighted by a Legendre polynomial $P_l(\hat{\mathbf{p}}\cdot\hat{\mathbf{z}})$ of the angular distribution of $\mathbf{p}$. This integral, $N_l(\varepsilon)$, is a coefficient of the expansion of the angular distribution $\int d\mathbf{r}\, N(\mathbf{r},\mathbf{p})$ into spherical harmonics of $\hat{\mathbf{p}}$ with arbitrary reference frame. Each coefficient $N_l(\varepsilon)$ obeys a separate equation analogous to (1) with a source term proportional to $P_l(\hat{\mathbf{p}}\cdot\hat{\mathbf{z}})$ and a kernel $k_{\varepsilon l}$ that depends on l as noted below.

This dependence on l causes the ratio $N_l(\epsilon)/N(\epsilon)$ to decrease with increasing l, thus representing the angular diffusion of $N(\mathbf{r},\mathbf{p})$ associated with degradation.

(c) Weighting the integral over $N(\mathbf{r},\mathbf{p})$ by powers of the space coordinates, in addition to $P_l(\hat{\mathbf{p}}\cdot\hat{\mathbf{z}})$, yields finally a network of equations analogous to (1) yielding the angular and spatial moments of $N(\mathbf{r},\mathbf{p})$. Note that the integrals over $\mathbf{r}$ or $\mathbf{p}$ considered here are observable, according to Ref. 8, even though $N(\mathbf{r},\mathbf{p})$ itself is not.

(d) The electron distribution itself is to be reconstructed from such moments complemented, if necessary, by data on the electron penetration to asymptotically high distances from the source.[3]

Studying initially the electron motion in an infinitely extended homogeneous medium[1-3] separates the effects of electron-medium interactions from those of boundaries, source distribution, and inhomogeneities. Source and boundary effects can be treated in step (d) provided the medium extends over many free paths. Otherwise they should be dealt with in a separate study together with the effects of inhomogeneities.

Within this framework we consider now the degradation kernel $k_\epsilon(\mathbf{q},\omega)$ in somewhat greater detail. We deal with a joint transition of an electron with momentum $\hbar\mathbf{p}_{\varepsilon'}$ [corresponding to energy $(\varepsilon = \hbar^2 p_{\varepsilon'}^2/2m)$] to a momentum $\hbar\mathbf{p}_\epsilon = \hbar(\mathbf{p}_{\varepsilon'} - \mathbf{q})$ and energy $\epsilon = \varepsilon - \hbar\omega$, and of the medium from a state n_0 to a state n. Its probability amplitude is represented by $p_{\varepsilon'}^{-1}(\mathbf{p}_\epsilon n|T|\mathbf{p}_{\varepsilon'} n_0)$, where $\mathbf{p}_{\varepsilon'} n_0$ $(\mathbf{p}_\epsilon n)$ labels the initial (final) state of the transition and T indicates a transition operator to be discussed elsewhere. (The matrix element of T is regarded here as dimensionless; its coefficient $p_{\varepsilon'}^{-1} = \lambda\!\!\!^{-}_{\varepsilon'}$ provides the dimension of a cross section when squared.) The corresponding probability, averaged over n_0 with thermal weight P_0 and summed over n (in Van Hove's notation[9]) is indicated by

$$W_{\varepsilon'}(\mathbf{p}_\epsilon\cdot\mathbf{p}_{\varepsilon'},\omega) = p_{\varepsilon'}^{-2} \sum_{n,n_0} P_0 |(\mathbf{p}_\epsilon n|T|\mathbf{p}_{\varepsilon'} n_0)|^2 \times \delta(\mathbf{p}_\epsilon - \mathbf{p}_{\varepsilon'} + \mathbf{q})\delta(\epsilon - \varepsilon + \hbar\omega) \ . \tag{2}$$

The isotropy of the medium causes (2) to depend on $\{\mathbf{p}_{\varepsilon'},\mathbf{p}_\epsilon\}$ through the invariant product $\mathbf{p}_\epsilon\cdot\mathbf{p}_{\varepsilon'}$. To determine finally the kernel $k_\epsilon(\mathbf{q},\omega)$ of (1), note that (1) deals with $N(\epsilon)$—an integral over the direction of $\mathbf{p}_\epsilon$—rather than with $N(\mathbf{p}_\epsilon)$. The kernel $k_{\varepsilon'}$ is accordingly obtained by averaging (2) *independently* over the directions of $\mathbf{p}_{\varepsilon'}$ and $\mathbf{p}_\epsilon$, as in Sec. 9 of Ref. 3. The result thus obtained from (2) has the proper dimensions provided the states $\{n,n_0\}$ are normalized per unit volume of the material.

The structure of (2) implies that the initial electron state is represented by the density matrix $\exp[i\mathbf{p}_{\varepsilon'}\cdot(\mathbf{r}' - \mathbf{r}'')]$, whose average over the direction $\hat{\mathbf{p}}_{\varepsilon'}$ yields the spherical Bessel function $j_0(p_{\varepsilon'}|\mathbf{r}' - \mathbf{r}''|)$. The dependence of this function on the distance $|\mathbf{r}' - \mathbf{r}''|$ represents the extent of delocalization of the electron as a function of the energy ε. The influence of delocalization looms increasingly large for the kernels $k_{\varepsilon l}(\mathbf{q},\omega)$ pertaining to the higher harmonic coefficients $N_l(\epsilon)$ of the angular distribution $N(\mathbf{p}_\epsilon)$ [item (b) above]. The kernel $k_{\varepsilon' l}$ derives from a coefficient in the expansion of $W_{\varepsilon'}(\mathbf{p}_\epsilon\cdot\mathbf{p}_{\varepsilon'},\omega)$ into harmonics $P_l(\hat{\mathbf{p}}_\epsilon\cdot\hat{\mathbf{p}}_{\varepsilon'})$. The averaging over the initial density matrix $\exp[i\mathbf{p}_{\varepsilon'}\cdot(\mathbf{r}' - \mathbf{r}'')]$ is then weighted by a harmonic of $\hat{\mathbf{p}}_{\varepsilon'}$ yielding a matrix $j_l(p_{\varepsilon'}|\mathbf{r}' - \mathbf{r}''|)$ which is $\ll 1$ for all distances $|\mathbf{r}' - \mathbf{r}''| \ll l\lambda\!\!\!^{-}_{\varepsilon'} = l p_{\varepsilon'}^{-1}$ and reduces the value of $k_{\varepsilon l}$ accordingly.

The structure factor emerges from (2) in the Born approximation where (2) splits into factors that depend separately on the medium and on the electron variables.[9] All coherence effects between successive interactions of the electron are represented here by non-Born contributions to the operator T of (2). More realistic treatments of $k_\varepsilon(\mathbf{q},\omega)$, considering even only the exchange of the incident electron with those of the medium, will require a deeper analysis to sort out its dependence on the separate properties of the electron and the medium. Success of this analysis would identify a new set of observable parameters of each material as targets for novel experimental study.

The process of electron degradation terminates when the energy ϵ has decayed to the thermal range. Indeed, the whole degradation process may be viewed as a relaxation of electron energy toward thermal equilibrium. Extensive studies of electron interaction with materials very near thermal equilibrium have been made in connection with experiments on drift mobility, where the equilibrium is perturbed weakly by an external electric field.[13] Several theoretical concepts and structures relevant to drift mobility will presumably prove relevant to the degradation and diffusion of slow electrons. Such are the fluctuation-dissipation relationship,[14] Kubo's representation of conductivity and of other macroscopic observables in terms of correlation functions,[15] and Zwanzig's introduction of irreversibility through the elimination of unobserved variables.[16]

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