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Comments on the x-ray edge and recoil problems*

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Some particular cases of the x-ray edge and recoil problems are examined. The usual independent-particle theory is evaluated exactly for the case in which the excitation introduces a full virtual level into the conduction band. These results make contact with studies of rare-gas pair absorption in metals and also afford a comparison wih earlier theories. Some aspects of the difficulties introduced by the electron-electron interactions in real metals are also discussed.

I. INTRODUCTION

During the course of the work described in the preceding four papers[1-4] a number of points have emerged concerning the theoretical description of local excitations in metals. These pertain both to the recoil problem, and the optical problem. In the recoil problem the metal adjusts to a suddenly applied local perturbation and creates electron-hole pairs in the process. In the analogous optical processes the metal absorbs a photon to create a core hole and leave the solid both locally excited and with the addition of propagating electron-hole pairs. It is the latter process that has direct relevance to the experimental studies of optical absorption by impurities in metals reported above. An approximation to the recoil problem arises in practice when a transition takes place within one core, and the electron gas suddenly experiences a modified local potential in that region. One principal effect of a local optical excitation is also to introduce a local potential due to the localized hole and its screen. Therefore the recoil problem is often regarded as a prototype problem and discussed at the same time as the optical process.

There are at present available in the literature the following predictions for the profile $f(E)$ of final states of energy E (above the threshold E_t) reached by recoil and by optical-excitation processes. For the recoil problem the predicted profile is[5]

$$f(E)=B(E-E_t)^{\beta}, \quad (E>E_t), \tag{1}$$

with

$$\beta=\sum_{l'} 2(2l'+1)\left(\frac{\delta_{l'}}{\pi}\right)^2-1 \tag{2}$$

and B constant. For the optical process the prediction for transition to the l partial wave of the distorted band function is[6,7]

$$f_l(E)=A_l(E)(E-E_t)^{-\alpha_l}, \quad (E>E_t), \tag{3}$$

with

$$\alpha_l=\frac{2\delta_l}{\pi}-\sum_{l'} 2(2l'+1)\left(\frac{\delta_{l'}}{\pi}\right)^2 \tag{4}$$

and $A_l(E)$ proportional to an energy-dependent one-particle optical matrix element. In each of these formulas the $\delta_{l'}$ are *changes* in l' wave phase shift at E_F induced by the transition from the initial to the final state. The factor 2 multiplying $\delta_{l'}$ in Eqs. (2) and (4) is replaced by a sum over spin in spin-dependent cases. The value of l in the optical process indicates the partial wave to which the optical operator couples the initially occupied core orbital.

The formulas (1)–(4) are derived for conduction-band particles that interact only with core holes [or the applied perturbation for Eqs. (1) and (2)]. These are in effect ΔSCF calculation [the threshold energy is taken as the difference in total energies of two self-consistent-field (SCF) calculations], as exhibited explicitly in the work of Combescot and Nozières, and of Friedel.[6] The profile described by Eqs. (1) and (2) arises wholly from orthogonality effects of the type discussed by Anderson and Hopfield.[5] An infinite density of low-energy electron-hole pairs are said to be created by excitations near threshold.

Some success has been achieved in attempts to explain experimental results using Eqs. (1)–(4). X-ray photoemission data from metals do often possess asymmetric profiles that can be fitted very accurately over several eV by convolutions of apparatus, lifetime, and phonon-broadening functions with Eq. (1) for some fitted value of β.[8,9] The accord seems less satisfactory in the comparison of experimental photon absorption and emission data with theory. Maxima observed near the L_{23} absorption thresholds of Na, Mg, Al have been ascribed to the lifetime broadened profile of Eq. (3) with α positive.[10] However, Dow and co-workers[11-13] have argued in a way we find convincing that a self-consistent fit between theory and all available experiments determining phase shifts is lacking in these cases. The absence of an explicable dependence of profile on momentum transfer in electron-scattering experiments[14] has been interpreted as further experimental evidence against the theory. In our own work, reported in the preceding papers, the theory fails to describe the absorption profile of rare-gas excitations in metals[15] in situations where the parameters relevant to the theory are rather well established.

The reason for these difficulties is not at present understood, since the experimental materials seem to conform as well as could be hoped in the constraints on the theory. One interesting point for further study is the complicated role of the electronic charge in the optical problem.[16] Thus, e enters both into the coupling of the initial orbital to the radiation field and into the correlation processes of the electron liquid. At the same time it determines the short-range electrostatic perturbation on the conduction states in the excited configuration, in addition to the charge shift required to achieve long-range electrical neutrality. It is far from self-evident that the several static and dynamical Coulomb correlation effects that are intrinsic to the local optical problem can possibly be simulated in detail by the ΔSCF method.

In the comments that follow we shall *not* provide exact solutions of either the recoil or optical problems for metals. We shall, however, present some exact results for the recoil problem that allow the recoil profile to be determined once the many-body ground-state wave function of the electron liquid is known. The profile apparently depends explicitly on the many-particle correlation functions of the conduction electron liquid, so that theories lacking Coulomb correlation effects cannot reproduce these effects exactly. There is no indication, however, that the corrections are large. These, and other comments related to the role of electron-electron interactions, are presented in Sec. III. The comments of Sec. II that follow immediately concern the special case of the ΔSCF approximation. In particular, some cases are examined for which the theory may be evaluated in a sensibly exact manner to yield a detailed insight into the meaning of the results. The important limit in which the coupling between the excited center and the conduction band tends to zero is also analyzed.

II. CASE OF INDEPENDENT PARTICLES

All the results of this section are obtained for the particular case in which the initial- and final-state wave functions of the solid are represented by Slater determinants of one-particle orbitals and the interactions among particles otherwise ignored. The orbitals in the initial state determinant are eigenfunctions of a Hamiltonian different from that of the excited-state orbitals. This is appropriate for the ΔSCF approximation in which Eqs. (1)–(4) are derived, the different Hamiltonians being a consequence of the local perturbation.

By neglecting all other effects of interaction among particles in the present section we employ precisely the model adopted in the early work of Friedel[6] and Anderson.[5] In this approach only the wave functions are required; model Hamiltonians that may reproduce the wave functions in various approximations are irrelevant. Our contribution is to evaluate the optical and recoil matrix elements *exactly* for model wave functions that conform closely to an important class of local perturbations. As recognized in much earlier work, the determinantal wave functions are determined by the phase shifts suffered by various orbitals scattering off the local center, presumed isotropic. To be specific, we need to identify the phase shifts as functions of energy for all relevant orbitals of both the ground and excited configuration.

The new results presented below are restricted to the case in which one phase shift increases by π at E_F in passing from the initial to the final configuration. It turns out that this restricted case not only provides exact predictions for comparison with Eqs. (1)–(4) but also has considerable relevance to two physical problems discussed in the experimental studies reported above. These are, respectively, (a) the optical absorption of molecular centers having magnetic excited states, and (b) the transition from band to localized orbitals in metallic systems.

A final point is that Eqs. (1)–(4) can be generalized beyond the isotropic sphere model used in their derivation. One merely replaces l by other quantum numbers that appropriately specify the symmetry groups of the one-particle orbitals in the particular problems. Spin-orbit coupling in the perturbed cell, or tetragonalities associated with core hole asymmetry, are, for example, easily accommodated by the use of correct channel labels. As a crude model of surface excitations, Fig. 1(b) shows the active site at the center of the circular face of a hemispherical piece of metal. For the usual boundary condition $\psi = 0$ at the metal "surface" the one-electron eigenfunctions for this problem remain those of the spherical problem but restricted now to spherical harmonics Y_{lm} maintaining a node on the circular face. The excitation still introduces phase shifts in these orbitals, and the formulas for the spherical problem hold for the surface problem but with summations extending over odd $(l+m)$ only. Note that the optical properties now have axial symmetry.

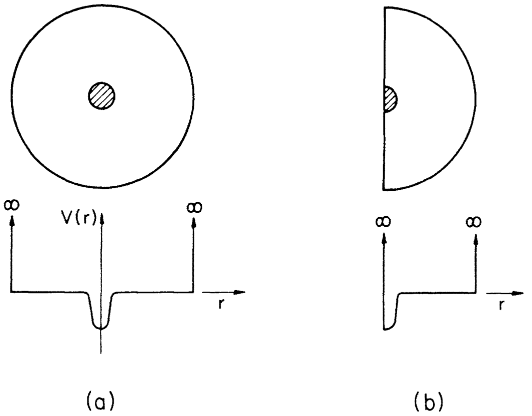

FIG. 1. Usual spherical model of a metal with a perturbation at its center may be modified as shown in (b) to give a model of surface absorption with no substantial change in the theory. A variety of alternative geometries are accessible.

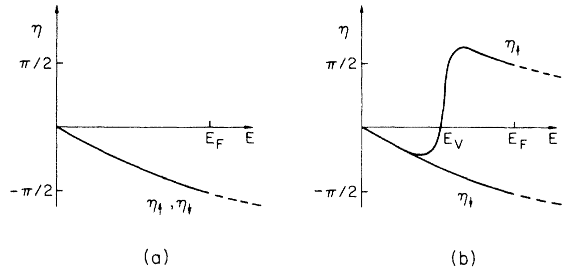

FIG. 2. (a) Phase shifts for spin-up and spin-down s waves at an empty cell screened only by s waves in a monovalent metal. (b) Same as (a) but with a full spin-up virtual level in the band at E_v; this represents the excited configuration discussed in Sec. II A.

A. Virtual level in the x-ray edge problem

The optical absorption takes a particularly simple form in the case for which the excitation has no effect other than to introduce a full virtual level into the conduction band. We show in what follows that the spectrum is a δ function for this case. To simplify the problem to its essentials and to make maximum contact with the experimental results presented above we shall specify the structures, and hence the phase shifts, for the ground and excited configurations, rather closely.

Figure 2(a) shows as a function of energy the phase shift of the one-electron s-wave orbitals in our chosen model ground configuration. Figure 2(b) shows the differing spin-up and spin-down s-wave phase shifts of the chosen excited configuration in which the spin-up subband is changed by the introduction of a virtual level. We shall presume that other partial waves remain unperturbed by the excitation, so that Fig. 2 contains *all* changes introduced by the optical process. The particular form chosen for the ground configuration of Fig. 2(a) shows s-wave charge repelled from the central cell, and the value $\eta_0 = -\frac{1}{2}\pi$ at E_F for both spin senses indicates from the Friedel sum rule that one electronic charge is removed from this location (i.e., $2\eta_0/\pi = -1$). This condition shows that Fig. 2(a) provides a satisfactory if crude model of an unrelaxed vacancy in metallic H or substitutional rare-gas impurity in the neighboring monovalent metal. The spin-down phase shift $\eta'_{0\downarrow}$ of the model excited configuration shown in 2(b) are unchanged from 2(a). However, the spin-up phase shift $\eta'_{0\uparrow}$ increases by an increment of π near the energy E_v of the virtual-bound state, and remains larger than $\eta'_{0\downarrow}$ by π at all $E > E_v$. This change of $\eta'_{0\uparrow}$ at E_F is required by the Friedel sum rule to screen the extra positive charge of a core hole in the excited configuration. Thus, the optical process has been simplified until its only effect is to create a core hole and to introduce a spin-up full virtual level at $E_v < E_F$. All phase shifts other than the spin-up s wave remain unchanged at E_F, and the latter changes by $\delta_{0\uparrow} = \eta'_{0\uparrow} - \eta_{0\uparrow} = \pi$. Note that multiples of π in the definition of η are assigned by counting the radial nodes in the orbital from $r = 0$ to a radius outside the impurity, and comparing the result with that in the pure host for the same orbital energy. Thus K in Cs has $\eta_0 = -2\pi$ since it lacks two radial nodes.

The effect of these changes on the one-electron s orbitals is clarified by Fig. 3. The orbitals of the ground configuration are indicated in Fig. 3(a), with those occupied in the state of lowest total energy marked by full circles. The full virtual level lowers by exactly the level spacing those orbitals at $E > E_v$ in the excited configuration. The excited configuration of least total energy is shown in Fig. 3(b), with all one-particle orbitals having $E < E_F$ full. A state of higher total energy containing one electron-hole pair excitation is shown in Fig. 3(c). Our objective in what follows is to show that the optical transition from a p-like core orbital in 3(a) to excited configurations of the type 3(b), 3(c), ... has a nonzero amplitude only to 3(b). The excitation spectrum is therefore a δ function, and added electron-hole pair creation processes are completely suppressed.

The proof is very simple: one need only realize that the orbitals near to and above E_F are *identical* in the ground and excited configurations. With $\delta = \pi$, the one-electron spin-up levels above the resonance are lowered in energy by the level spacing but the added electron fills the band *exactly* back to E_F. The orbitals of the two configura-

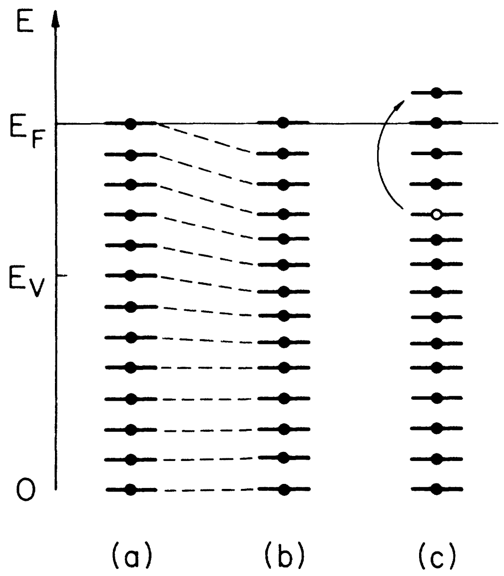

FIG. 3. One-particle spin-up energy levels (a) in the ground configuration; (b) in the excited configuration [see Fig. 2(b)]; (c) same as (b) but with a pair excitation.

tions near to and above E_F have equal energies and are identical outside the impurity cell. It has been the practice in all previous treatments to neglect central cell corrections in the calculation of matrix elements. This neglect is particularly well justified in the present case because all orbitals above the virtual level have almost zero amplitudes in the central cell in both the ground and excited configuration.

To use Hartree-Fock theory we construct the determinant Φ_0^0 of the N lowest conduction orbitals of the ground configuration [Fig. 3(a)] together with the relevant core orbital ψ_0^0. Similarly, we construct the determinant $\Phi(q, r, \ldots; s, t \ldots)$ of $N+1$ orbitals from the excited configuration in which orbital $q, r, \ldots,$ with $E \leq E_F$ are empty and $s, t, \ldots,$ with $E > E_F$, are occupied. Then $\langle \Phi_0^0 | \Phi(q, r \ldots; s, t \ldots)\rangle \equiv 0$ whenever $s, t, \ldots$ exist since $s, t, \ldots$ belong also to the ground configuration and are therefore orthogonal to all occupied orbitals of Φ_0^0. Thus Φ_0^0 is orthogonal to all Φ except the lowest member Φ_0.

To study more generally the matrix elements of operators connecting Φ_0^0 to the Φ we note that the N occupied band orbitals of Φ_0^0 can be synthesized from the $N+1$ occupied orbitals of Φ_0. This happens because the ground and excited configurations give rise to different complete sets of band orbitals ψ_i^0, $i = 1, 2 \ldots,$ and ψ_j, $j = 0, 1, 2 \ldots,$ whose members *un*occupied in Φ_0^0 and Φ_0, being common to the two sets, cannot enter into a description of Φ_0^0. By unitary transformation that leaves its value unchanged Φ_0 may therefore be rotated into the determinant of the N band orbitals of Φ_0^0 together with a final orbital ψ_L which must, from the exclusion principle, be quasilocalized. To supplement the preceding demonstration that Φ_0^0 is orthogonal to all except the lowest Φ we may now write down the result

$$\langle \Phi_0^0 | \Phi_0 \rangle = \langle \psi_0 | \psi_L \rangle = 0 , \tag{5}$$

to indicate that the necessary *exact* orthogonality of the two configurations Φ_0^0 and Φ_0 arises from the orthogonality of the local orbitals ψ_0 and ψ_L; *the overlap in the electron gas is unity.*

In an analogous manner we find the matrix elements of the optical operator to be zero for all except the lowest excited configuration, for which the δ-function absorption amplitude is

$$\langle \Phi_0^0 | \sum_i \nabla_i | \Phi_0 \rangle = \langle \psi_0^0 | \nabla | \psi_L \rangle . \tag{6}$$

Of course, the optical operator also couples excited states of Φ^0 to Φ_0^0, but these do not belong to the configuration Φ; they are instead the carrier excitations of the ground configuration.

It is worth noting here that the condition $\delta = \pi$ cannot, in practice, be maintained for all $E > E_F$, as presumed above, since η, $\eta' \to 0$ as $E \to \infty$ by definition. This has no effect on the threshold δ function but does mean that other, diffuse, absorption must occur at higher energy by the excitation of members of Φ containing orbitals ψ *not* phase shifted from ground-state orbitals ψ^0 by π.

In summarizing these results we note that an excitation whose only effect is to introduce a full virtual level has a δ-function absorption spectrum. This is the result employed in the preceding papers to interpret the molecular spectra of rare-gas pairs in metals.[2,4] We note that for this particular case of a virtual level the spin-dependent analogs of Eqs. (3) and (4) predict for a $p \to s$ transition the exponent

$$\alpha_0 = 2\delta_{0\uparrow}/\pi - (\delta_{0\uparrow}/\pi)^2 = 1 ,$$

so that

$$f(E) = A(E - E_t)^{-1} \quad (E \geq E_t) . \tag{7}$$

A similar E^{-1} divergence of Eq. (1), in the recoil problem for $\beta \to 1$, has previously been shown to represent a δ function,[17] and the identical result holds in the interpretation of Eq. (7) from the proportionality of absorption to $\mathrm{Im}(\omega - E_t - i\delta)^{-\alpha}$ (see Ref. 6). The present derivation provides, in addition, the constant of proportionality and includes explicitly an energy dependence of the phase shifts. The result supports our assignment of the pair spectra reported in Paper II to a sharp virtual level, and confirms through Eq. (6) that the expected oscillator strength should be comparable with that of the atomic and molecular resonance lines.

B. Weak-coupling limit

There is no reason to suppose that a local center in a metal can support excited configurations of one type, say Φ, alone. Indeed there exists a compelling reason, in some cases, to believe that a center can occupy any of an indefinitely large set $\Phi, \Phi', \Phi'', \ldots$ of different families of excited configurations. The configurations $\Phi', \Phi'', \ldots$ differ from Φ in that they contain localized orbitals $\psi'_L, \psi''_L, \ldots$ (or possibly several) that differ from ψ_L and are orthogonal to it. The reason that this must be so is that the *atomic* excitation spectrum of an atomic center must eventually be recovered as its coupling to the electron gas is reduced. In this limit the ψ'_L tend towards the atomic orbitals of the central atom. A particular family, say Φ', of composite states of the metal plus atom thus comprises the atom with ψ' interacting with the metal ground state, and similar composite states derived from this by the excitation of quasiparticle in the metal.

Questions related to the excited configurational lifetime enter at this point. Clearly, the notion of discrete families of excitations, each built from a separate basic configuration of the atom plus ground state metal by the excitation of electron-hole pairs, loses its meaning when the excited state lifetimes become so short that the different families can no longer be distinguished. The demonstration in a preceding paper[2] that d-like structure remains in the Xe spectrum at dilution in K provides a first example of distinct excitation families for simple impurities in metals.

It is interesting to speculate on the way an excitation spectrum must mutate as the center is brought into increasingly strong contact with a Fermi liquid. In the weak-coupling limit there must occur the analog of Wigner localization in which Coulomb correlations prevent hybridization as the local state remains spatially separated from the host band states. With increased coupling the atomic levels must exchange electrons with the Fermi ball reservoir but, since Coulomb correlations remains strong, each local orbital probably exists as a virtual bound state. Up to this point the excitation spectrum maintains a δ-function form in accordance with Sec. II A. This character is lost, in general, when the atomic couplings break down and the different atomic configurations mix. Finally, in the strong coupling limit, the spin magnetism induced by the difference of the spin-parallel and spin-antiparallel correlation energies breaks down.

C. Virtual level in the recoil problem

It is equally simple to carry through the *recoil* problem for the case in which the local potential introduces a virtual level into the excited configuration. The added electron contributed by the optical process considered in Sec. II A is now lacking and *all* members of the excited configuration are now orthogonal to the initial configuration. The recoil spectrum thus extends with zero amplitude from threshold up to infinite energy. In practice, a diffuse absorption must occur well above threshold, as in Sec. II A, because δ necessarily departs from π at sufficiently large one-particle energies. Figure 4 shows the configurations.

Note finally that Eqs. (1) and (2) predict for this particular process that $\beta = 0$, so that $f(E)$ takes the constant value

$$f(E) = B \quad (E > E_t) . \tag{8}$$

This has often been understood to mean that the spectrum has a step-function threshold at E_t. Our example, to the contrary, identifies the value of B as zero. It will be equally evident that this exact orthogonality prevails whenever the phase

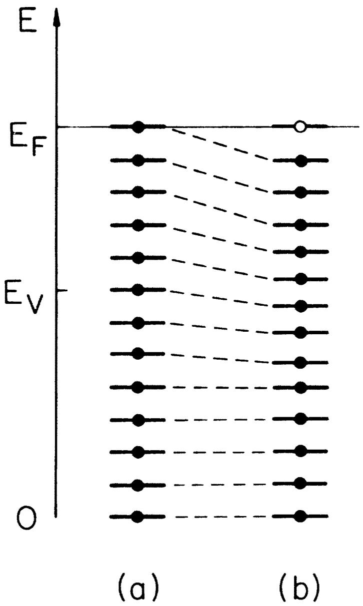

FIG. 4. When the ground state (a) is modified by the creation of a virtual level (b) the recoil profile has zero amplitude near threshold because an orbital occupied in the unperturbed system must be unoccupied in the perturbed configuration.

shift at E_F changes by a nonzero *multiple* of π. It has previously been recognized that B tends to zero in the special case for which the conduction electron density is vanishingly small.[6]

III. INFLUENCE OF ELECTRON-ELECTRON INTERACTIONS

When Coulombic interactions are added to the independent particle model discussed above, the theory becomes much more complex and in fact the problem of predicting profiles has remained largely unsolved. Whatever the influence of Coulomb correlations on the x-ray and recoil profiles may be, it is *certain* that the effect on the threshold energy E_t is large compared with the typical energies ~1 eV of solid state chemistry. This is so much the case that atomic ideas yield a far better account of the threshold energy than that provided by one-electron band-structure ideas. The problem is not that one-electron theory, when used correctly, is inadequate, for Hartree-Fock methods are able to predict deep core thresholds to ~2% in some cases.[18] Rather, it is the Koopmans theorem that fails, so that the band structure of the perfect crystal becomes largely irrelevant to the energy of the excited configuration. In what follows we discuss these effects briefly before turning to questions involving the profile above threshold.

A. Threshold for core excitations

The difficulty with one-electron band schemes is that the energy required to excite an electron from one-electron energy E_i to energy E_f is not always equal to $\hbar\omega = E_f - E_i$. Rather, the required energy is the difference in *total* energy between the two configurations, and the difficulty centers on the fact that the total energy is not just a sum of one-electron energies. This discrepancy is often (somewhat obscurely) mentioned under the name "final-state interactions" and the size of the error regarded as the interaction between the excited state and the hole in the final configuration. To the writer it appears that this language lacks utility, as all one-electron levels are changed by the excitation. Even in the case of atomic excitations the one-electron energies serve only to provide crude estimates of the change in total energy accompanying electron promotion. It is just the same in crystals whenever the excited electron becomes localized near the hole. The hole field deforms the conduction band and so causes a violation of the Koopmans theorem. The true excitation energies fall well below the relevant differences of one-electron energies that emerge from band structure calculations.

The necessary calculations for the ground and excited self-consistent configuration can be carried out to yield core excitation energies in metals accurate to a fraction of 1 eV for excitations requiring ~100 eV.[19] The energy contribution from the "electron-hole interaction" arises in metals from the fact that the conduction band deforms to screen the localized hole; it amounts typically to 4–7 eV, and this provides the principal measure of deviations from the band structure picture.

We emphasize, however, that true "solid state" effects on the excitation energy total to a much smaller value, typically ~1 eV. This could be demonstrated directly if the atomic transition energies were known, but this is often not the case. We therefore present a simple method by which atomic core hole energies may be estimated for comparison with the excitation energy in solids. Consider by way of example the atomic $1s^2 2s^2 2p^6 3s \to 1s^2 2s^2 2p^5 3s^2$ transition energy of Na. We first ionize Na to $1s^2 2s^2 2p^6$, requiring energy $\mathcal{I}_1$, and then to $1s^2 2s^2 2p^5$, requiring work $\mathcal{I}_2$. But for weakly bound states, the Na^{++} core is almost equivalent to the Mg^{++} $1s^2 2s^2 2p^6$ core, and the energy required to place two $3s$ electrons on Na^{++} is $-\mathcal{I}_1' - \mathcal{I}_2'$ in which primes indicate the ionization potentials of Mg. The atomic excitation energy is thus

$$\hbar\omega(\text{Na}2p \to 3s) = \sum_{i=1,2} \delta\mathcal{I}_i , \tag{9}$$

with $\delta\mathcal{I}_i = \mathcal{I}_i - \mathcal{I}_i'$. This prescription may be generalized to

$$\hbar\omega = \sum_{n} \delta\mathcal{I}_i , \tag{10}$$

with $n-1$ the number of electrons in the ground state with energy greater than that excited by the transition, and $\delta\mathcal{I}_i$ the difference in ith ionization potential between the test atom and its neighbor to the right in the Periodic Table.

Table I compares the prediction of this model with some observed transition energies in crystals. The ionization energies were obtained from standard sources.[20] The close agreement measures both the accuracy of this model of atomic excitations and the rather small influences of solid state effects on the transition energies. Figure 5 shows how the residual solid state effects may be represented by cohesion shifts of the total energies of the two configurations, e.g., of Mg and Na for the case of Na $2p$ excitations on immersion in the relaxed solid, and finally an excited-state Stokes shift. The first effect is unlikely to exceed ~1 eV, and the second may dominate to produce somewhat larger deviations of predictions to the small side

TABLE I. Observed threshold energies E_t of some metals compared with the predicted atomic-transition energies given by $\sum \delta \mathcal{G}$ of Eq. (10).

	Li	Be	Na	Mg	Al	Si
$\mathcal{G}_1$	5.39	9.32	5.14	7.64	5.98	8.15
$\mathcal{G}_2$	75.62	18.21	47.29	15.03	18.82	16.34
$\mathcal{G}_3$	⋯	⋯	⋯	80.12	28.44	33.46
$\mathcal{G}_4$	⋯	⋯	⋯	⋯	119.96	45.13
$\sum \delta \mathcal{G}$	53.48	⋯	29.75	49.55	70.13	⋯
E_t	54.7	⋯	30.7	49.6	72.9	⋯

of observation in cases where the excited state misfit is large.

In summary we note that band-structure schemes provide a poor starting point for a discussion of core-hole thresholds. Solid state effects are in fact small, typically ~1 eV, and the threshold can be predicted to this accuracy using atomic ionization potentials alone, with no reference to solid state properties. The method outlined above admits obvious and useful extentions to the prediction of energy *differences* among various observed transitions of one species, and also to multiply excited states of atoms in crystals.

B. Recoil profile

The recoil problem provides a prototype of local perturbations on a Fermi liquid and is in some degree tractable. In this problem, believed relevant to transitions internal to one core of the lattice, the mobile conduction electron system is subject to a sudden perturbation that simulates its modified interaction with the core that undergoes the transition. The Hamiltonian of the N-particle liquid is, as usual,[21]

$$\mathcal{H}_0 = -\sum_{n=1}^{N} \frac{\hbar^2}{2m} \nabla_n^2 + \frac{1}{2} \sum_{\substack{n' \\ n' \neq n}} \frac{e^2}{|r_n - r_{n'}|} + V_0 ,$$

V_0 being the neutralizing background potential. We shall write the perturbing potential suddenly experienced by the liquid as $V = \sum_n V(\vec{r}_n)$ with the index n running over all N electrons, with positions $\vec{r}_n$, in the N-electron band. $V(\vec{r}_n)$ is evidently a short-ranged potential, since the core charge remains unchanged in the transition.

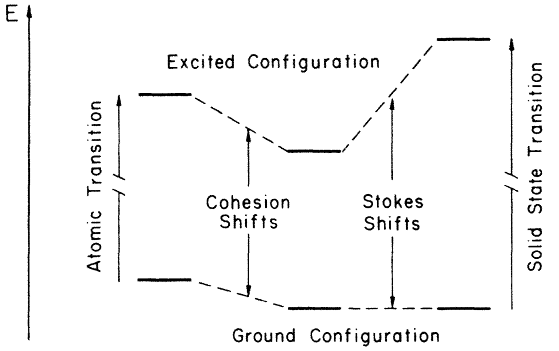

FIG. 5. Evolution of the threshold energy from the atomic-transition energy, through cohesion shifts of the ground- and excited-state energies and the excited-state Stokes shift.

Suppose that the system initially occupies state Φ_i^0 of the N-electron system (an eigenstate of $\mathcal{H}_0$), and that the eigenstates of $\mathcal{H} = \mathcal{H}_0 + V$ in which the system may finally be observed are Φ_j. Then, for a potential applied suddenly, the probability P_j that the system shall be found in state Φ_j is $P_j = |\langle \Phi_i^0 | \Phi_j \rangle|^2$. The spectrum of final state energies is therefore

$$\begin{aligned} f_i(E) &= \sum_j P_j \delta(E - E_j) \\ &= \sum_j |\langle \Phi_i^0 | \Phi_j \rangle|^2 \delta(E - E_j) , \end{aligned} \tag{11}$$

with

$$E_j = \langle \Phi_j | \mathcal{H}_0 + V | \Phi_j \rangle , \tag{12}$$

Now it is often more convenient to calculate the moments of $f(E)$ than the function itself, and this is the method by which we proceed. The pth moment is, by definition

$$\begin{aligned} \langle E^p \rangle = \sum_j P_j E_j^p = \sum_j & |\langle \Phi_i^0 | \Phi_j \rangle|^2 \\ & \times \langle \Phi_j | (\mathcal{H}_0 + V)^p | \Phi_j \rangle , \end{aligned} \tag{13}$$

which may be expanded as

$$\begin{aligned} \langle E^p \rangle = \sum_j \sum_{j'} & \langle \Phi_i^0 | \Phi_j \rangle \\ & \times \langle \Phi_j | (\mathcal{H}_0 + V)^p | \Phi_{j'} \rangle \langle \Phi_{j'} | \Phi_i^0 \rangle , \end{aligned} \tag{14}$$

since Φ_j, $\Phi_{j'}$ are eigenstates of $\mathcal{H}_0 + V$, so that finally

$$\langle E^p \rangle = \langle \Phi_i^0 | (\mathcal{H}_0 + V)^p | \Phi_i^0 \rangle . \tag{15}$$

The zeroth moment ($p = 0$) is clearly unity as should be the case for a normalized spectrum.

Equation (15) is *exact* for the precisely defined recoil problem when the exact wave function and Hamiltonian are used. One encounters customary commutation difficulties for $p \geq 3$, but for $p = 1$ and 2 the evaluation is simplified by the fact that Φ_i^0 is an eigenstate of $\mathcal{H}_0$. The right-hand side becomes $\langle \Phi_i^0 | (E_i^0 + V)^p | \Phi_i^0 \rangle$ ($p = 1, 2$), so that the moments with respect to the energy $E_i^0 = \langle \Phi_i^0 | \mathcal{H}^0 | \Phi_i^0 \rangle$

of the initial state are

$$\langle (E - E_i^0)^p \rangle = \langle \Phi_i^0 | V^p | \Phi_i^0 \rangle \quad (p = 0, 1, 2) . \tag{16}$$

All the moments of a function are required to define the function fully, but turns out that the two cases $p = 1$ and 2 give much qualitative insight into the recoil spectrum. Our objective in these remarks is to present this insight rather than performing detailed calculations for particular cases.

Consider first the case $p = 1$. One finds that the mean energy change $\langle E - E_i \rangle$ is *exactly* the first-order perturbation expression for the energy change $E_i^{(1)}$, of the initial state i. This result is to be expected, since at $t = 0+$ the system finds itself in Φ_i^0 with a perturbation V, as in well-known theories of optical transitions in insulators. For weak perturbations on the ground state $i = 0$, with $E_0^{(1)} \simeq E_t$, and E_t the threshold energy represented by the lowest eigenstate of $\mathcal{H}_0 + V$, this result shows that the recoil spectrum must be sharply peaked near E_t (see Fig. 6). There is no other way in which the *average* energy can fall so near E_t when M_2 shows that $f(E)$ extends past E_0^0 (see below) ~V above threshold. For strong perturbations, however, when first-order perturbation theory provides a poor approximation to E_t, the spectrum still centers on $E_0^{(1)}$ while the threshold at E_t lies at the much lower exact energy, E_0 of Φ_0. In this way the meaning of Anderson's "orthogonality catastrophe" becomes very clear: for large perturbations the system has little or no chance of exchanging exactly the correct energy with the perturbing field to project from its initial state to the ground state of $\mathcal{H}_0 + V$.

The second moment $p = 2$ gives further exact insight into the spread of the distribution around $E_0^{(1)}$. The diagonal matrix elements of $V^2 = [\sum_n V(r_n)]^2$ contain two types of terms: $\sum_n [V(r_n)]^2$ and $\sum_n \sum_{n' \neq n} V(r_n) V(r_{n'})$. Of these, the first is a one-electron operator and the second a two-electron operator. It is the latter that first introduces exchange and Coulomb correlations into a description of the recoil profile. Correlation tends to prevent two particles from simultaneously occupying the volume of the local perturbation. Therefore, correlation decreases the spread of the recoil spectrum as measured by the second moment by decreasing the value of $\langle V(r_n) V(r_{n'}) \rangle$ for $n \neq n'$. We note that in general the pth moment contains the p-particle correlation functions that describe the ground state $i = 0$. It is therefore clear that the recoil profile can only be reproduced accurately for any perturbing potential by the use of wave functions that contain the correct interparticle correlations. Determinantal wave functions that lead to Eqs. (1)–(4) contain a substantial part of the correlation between particles having parallel spins but ignore other correlations that arise from Coulombic interactions.

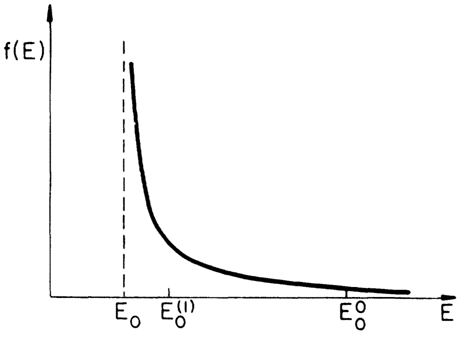

FIG. 6. Recoil spectrum for weak perturbations. The profile centers on the first-order perturbation energy $E_0^{(1)}$ of the ground-state wave function when exposed to the perturbing potential, which must lie close to the threshold E_t when the perturbation is weak. However, the second moment shows that the spectrum spreads past the initial energy E_0^0, giving the line an asymmetrical shape.

A simple example will serve to illustrate the content of Eq. (16). To the ground state of a uniform N-particle Fermi liquid of volume $N\Omega$ we shall suddenly apply a potential V that is uniform over a spherical volume Ω' and zero outside. The moments of the recoil profile with respect to the initial-state energy are, from Eq. (16),

$$\begin{aligned} &M_0 = 1 , \quad M_1 = V\Omega'/\Omega , \\ &M_2 = V^2[(\Omega'/\Omega) + \tfrac{1}{2}(\Omega'/\Omega)^2(\alpha + \beta)] . \end{aligned} \tag{17}$$

In M_2 the first term arises from one-particle terms and the second from two-particle terms, with

$$\alpha = V^{-2} \sum_{n \neq n'} \langle V(r_{n\uparrow}) V(r_{n'\uparrow}) \rangle$$

and

$$\beta = V^{-2} \sum_{n \neq n'} \langle V(r_{n\uparrow}) V(r_{n'\downarrow}) \rangle$$

both unity when correlations are absent. Two special cases may usefully be examined.

a. $\Omega' = \Omega$. In this case the extent of the perturbing field is comparable with the atomic cell size. The first moment exactly cancels the one-particle contribution to M_2 to leave the *second moment with respect to the mean*, namely, M_2' given by

$$M_2' = \tfrac{1}{2} V^2 (\Omega'/\Omega)^2 (\alpha + \beta) . \tag{18}$$

Although all one-particle terms thus vanish from M_2' for this case, the second moment is *not* radically modified by correlation. The Hartree approximation lacks correlation and gives $M_2' = V^2$. Determinantal wave functions have $\beta = 1$, and α is readily calculated to be $\alpha \simeq \frac{1}{2}$ for $\Omega' = \Omega$, independent of density, so $M_2' \simeq \frac{3}{4}V^2$. The Coulomb correlations of charged electron liquids are density dependent, but in the density range relevant to real metals are much less effective than exchange and lower M_2' further by only some 10%. Thus, as far as can be judged from the first three moments, Coulomb correlations cause no gross changes in the recoil spectrum for perturbations extending over volumes comparable with Ω. They merely cause a small reduction of the second moment. The changes of *profile* are, of course, not determined by these results.

b. $\Omega' \to 0$ *with* $\Omega' V$ *finite*. This is the case studied in many approaches that employ model Hamiltonians with δ-function perturbations. We shall identify the nonphysical consequences that this particular form of perturbation produces. With $\Delta = V\Omega'$ the integrated perturbation strength we find, from Eq. (16),

$$M_0 = 1\,, \quad M_1 = \Delta/\Omega\,, \qquad M_2' = (\Delta/\Omega)^2[(\Omega/\Omega') + \tfrac{1}{2}(\alpha + \beta - 2)]\,. \tag{19}$$

The second moment evidently diverges as $\Omega' \to 0$, owing to one-particle terms alone, and it is readily verified that a similar divergence occurs in all higher moments. It is clear that one-particle terms must indeed always dominate M_2' for $\Omega' < \Omega$, since $|(\alpha + \beta - 2)| \leq 1$. However, M_2' indicates that physically realistic potentials have recoil profiles that cut off at $E - E_t \sim \Delta(\Omega'\Omega)^{-1/2} = V(\Omega/\Omega')^{1/2}$, whereas the δ-function profile, if power law in form, must fall off as E^{-2} or slower for large E.

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