Transition from Adiabatic to Sudden Excitation of Core Electrons

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A model based on time-dependent quantum mechanics is presented for calculating the crossover from the adiabatic to the sudden regime in core ionization. With reasonable parameters the predictions of this model are in agreement with newly reported experimental results on shakeup as well as with older data on shakeoff.

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Measurements reported by Stöhr, Jaeger, and Rehr[1] on core ionization of N_2 adsorbed on nickel show that the shakeup satellite intensity is close to its high-energy value at energies only 15 eV above the nitrogen 1*s* threshold. They conclude from this result that the transition from adiabatic to sudden excitation is abrupt and essentially complete within this 15 eV. A simple theoretical model is in agreement with their experimental results. Their work represents the first systematic study of a well-defined, pronounced core-level shakeup peak in the expected transition region between adiabatic and sudden excitation.

Their theoretical approach correctly points out that the shakeup energy, ΔE, and the energy excess above threshold, E_{ex}, play key roles in determining whether the ionization is adiabatic or sudden. In addition, the calculations based on their model fit the data. In spite of this success, the model must be rejected as a description of the transition from adiabatic to sudden behavior. Furthermore, because the expression that they have derived from this model for the shakeup probability is based on incorrect approximations, it does not even accurately represent the proposed model.

Their model, which uses single-configuration wave functions and focuses on the interference between direct and conjugate shakeup to produce the energy dependence of shakeup, does not properly examine the factors that govern the transition from the adiabatic to the sudden limit. First, correlation between the outgoing electron and the remaining atomic electrons will be very strong when the transition is adiabatic. A satisfactory description of the adiabatic limit and the transition from this to the sudden limit must take this correlation into account. Such correlation cannot be adequately described by a single-configuration wave function. Second, a correct model for the transition from adiabatic to sudden regimes should be independent of the mechanism of ionization. (Shakeup is important in radioactive decay, where conjugate shakeup is impossible.) The correlation between the outgoing electron and the spectator electrons can be rigorously described by a suitable configuration-interaction calculation. At a lower level, the correlation can be treated approximately with time-dependent perturbation theory, the perturbation being the changing potential due to the departing electron.

I describe here such a model. It is more general than that proposed by Stöhr, Jaeger, and Rehr and agrees satisfactorily not only with their experimental data but also with the shakeoff data of Carlson and Krause.[2] However, my goal is not so much to obtain detailed agreement with the experimental results as to show that a time-dependent treatment with reasonable parameters does predict a rapid transition from adiabatic to sudden behavior. This conclusion is in agreement with the conclusions reached by Stöhr, Jaeger, and Rehr and in contrast to the common view, noted by them, "of a smooth transition with the sudden limit being reached about 200 eV above threshold.[1]"

Before developing the time-dependent model, it is useful to consider briefly the model proposed by Stöhr, Jaeger, and Rehr. They have observed that conjugate shakeup[3] may play an important role at energies slightly above threshold. (Direct shakeup is, for example, the dipole ionization of a carbon 1*s* electron in carbon monoxide with simultaneous monopole excitation of a valence electron from the occupied 1π to the vacant 2π orbital. The corresponding conjugate process is dipole excitation of the 1*s* electron to the vacant 2π orbital with simultaneous monopole ionization of a 1π electron.) It is quite likely that conjugate processes are important. We have recently found evidence to suggest that this is the dominant shakeup process in carbon monoxide near threshold.[4] However, the expression presented by Stöhr, Jaeger, and Rehr is based on incorrect

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approximations and cannot give the correct energy dependence for conjugate shakeup. First, they have chosen to ignore the energy dependence of the dipole matrix element for core ionization. This, however, varies as $E_{\mathrm{ex}}^{-3/2}$,[5] that is, at a slower, but not negligible, rate compared to the valence shakeoff matrix element, which goes as E_{ex}^{-2}.[1] Second, they assume that the ratio of conjugate to direct matrix elements is unity at the shakeup threshold. The purpose of their assumption is to force the shakeup intensity at threshold to zero. It is both unnecessary and unjustified; it is possibly incorrect. The cross section for shakeup will go to zero at threshold because of the vanishing of phase space available to the zero-energy ejected electron. There is, therefore, no need to invoke special conditions to bring the shakeup intensity to zero at threshold. In the plane-wave, hydrogenic-wave-function approximation used by Stöhr, Jaeger, and Rehr,[1] the direct matrix element goes to zero at threshold.[5] The conjugate matrix element, however, approaches a finite value.[5] It is, therefore, quite possible that, contrary to their assumption, shakeup is dominated by the conjugate process near threshold.

We turn now to a time-dependent model to describe the transition between adiabatic and sudden behavior. The interaction between the outgoing electron and the remaining electrons, which leads to shakeup, is treated explicitly, although approximately, via a time-dependent potential. Correlation among the other electrons is implicitly included, but in the approximation used here is ignored.

The sudden approximation will be valid if $t_0\Delta E/\hbar$ (the adiabaticity parameter) is much less than 1.[2,6,7] Here ΔE is the shakeup energy and t_0 is a characteristic time for the emission process. Conversely, the process will be adiabatic if $t_0\Delta E/\hbar$ is much greater than 1. The quantity t_0 is the time during which the potential changes and is therefore the time for the ejected core electron to move a distance of the order of atomic dimensions It is approximately proportional to $E_{\mathrm{ex}}^{1/2}$, where E_{ex} is the excess energy above threshold (kinetic energy of the ejected electron). The adiabaticity, therefore, depends on $\Delta E/E_{\mathrm{ex}}^{1/2}$ rather than on $\Delta E/E_{\mathrm{ex}}$, as proposed by Stöhr, Jaeger, and Rehr.

Using standard time-dependent quantum mechanics,[6] we can establish an expression for understanding the transition from adiabatic to sudden behavior. We let $a_k(t)$ represent the amplitude for the system to be in state k at time t. Then[6]

$$\dot{a}_k = \sum_{n\neq k} \frac{a_n}{\Delta E_{kn}} \exp\left(i\int_0^t \frac{\Delta E_{kn}}{\hbar}\,dt'\right)\left(\frac{\partial H}{\partial t}\right)_{kn}. \quad (1)$$

H is the time-dependent Hamiltonian of the system.

We take $a_0(-\infty)=1$ and $a_n(-\infty)=0$ for $n\neq 0$. As a first approximation assume that a_0 remains close to 1 and all other a's remain close to zero. The shakeup transition energy, ΔE, is taken to be independent of time. The potential energy terms in the Hamiltonian change during the ionization because of the disappearance of one core electron. Accordingly, we approximate H as $H^0 - Vf(t)$, where H^0 is the Hamiltonian of the original system, V is the potential due to the ejected core electron, and $f(t)$ goes from 0 at $t=-\infty$ to 1 at $t=\infty$, with the transition taking place over a time interval of t_0. For mathematical convenience, let $f(t)$ be the error function. Then $\partial H/\partial t$ is Gaussian in time with a width parameter equal to t_0.

With these simplifications,

$$\dot{a}_k = \frac{V_{k0}}{\Delta E_{k0}} \frac{1}{(2\pi)^{1/2} t_0} \exp\left(-\frac{t^2}{2t_0^2}\right) \exp\left(i\,\frac{\Delta E_{k0} t}{\hbar}\right), \quad (2)$$

where V_{k0} is the matrix element of V between states k and 0. Integrating from $-\infty$ to $+\infty$ and squaring gives the shakeup intensity, μ;

$$\mu^k = |a_k|^2 = |V_{k0}/\Delta E_{k0}|^2 \exp(-t_0^2\Delta E_{k0}^2/\hbar^2). \quad (3)$$

The quantity $V_{k0}/\Delta E_{k0}$ can be identified, via first-order perturbation theory,[8] with the usual Franck-Condon-type matrix element that gives the intensity of the shakeup transition in the sudden limit, μ_∞^k. This limit is reached when $t_0\Delta E_{k0}/\hbar$ is small.

The treatment of $f(t)$ used here is similar to that used by Gadzuk and Šunjić[9] in their analysis of line shapes in the transition region. They have, however, used an exponential rather than Gaussian form for $\partial H/\partial t$. The actual functional form is, however, not critical. The essential feature is that $\partial H/\partial t$ is zero except near $t=0$, where it is positive for some short time, t_0. The Gadzuk-Šunjić form as well as other simple forms for $\partial H/\partial t$ all lead to a dependence of adiabaticity on $t_0\Delta E_{k0}$, the product of the shakeup excitation energy and the length of time that the perturbation is turned on.

The quantity t_0 is, as noted above, the time for the ejected electron to move a distance comparable to atomic dimensions. Letting r represent this distance and making a simplifying approximation of constant velocity for the ejected electron gives

$$\mu = \mu_\infty \exp(-mr^2\Delta E^2/2\hbar^2 E_{\mathrm{ex}}), \qquad (4a)$$

$$= \mu_\infty \exp(-r^2\Delta E^2/15.32 E_{\mathrm{ex}}), \qquad (4b)$$

where the subscripts k and 0 have been dropped. The constant has been evaluated for r in angstroms and energies in electronvolts.

Figure 1 illustrates the application of Eq. (4) to the data of Stöhr, Jaeger, and Rehr. For this calculation, μ_∞ is the x-ray photoemission spectroscopy value of 0.55 and ΔE is 5 eV, as given by Stöhr, Jaeger, and Rehr. Curves calculated for $r = 1.5$ and 3.0 Å bracket the experimental points and fit the data at least as well as does the theoretical curve given by Stöhr, Jaeger, and Rehr. The values of r required for this agreement are plausible. These results show, in agreement with conclusions of Stöhr, Jaeger, and Rehr, that the onset of the sudden limit is abrupt and is determined by the low value of ΔE.

In Fig. 2 the predictions of Eq. (4) are compared with the neon shakeoff data of Carlson and Krause.[2] For this calculation, ΔE is 47.3 eV (the second ionization potential for sodium, which should be approximately equal to the valence ionization potential of core-ionized neon) and r is 0.51 Å,[10] the mean radius of the neon $2p$ shell, a value suggested by Carlson and Krause.[2] Only the asymptotic value of μ, 0.158, has been taken from the data.[2] The agreement between theory and experiment is reasonably good, the most serious failure being at low energies. The calculated value does not go to zero at the threshold for shakeoff and hence gives unrealistically high values at low energies. It should be noted also that the calculation includes all core *excitations* accompanied by shakeoff, whereas the experiment measures only core *ionizations* accompanied by shakeoff.

The model outlined above contains several major simplifying approximations. Among these are the functional form for $\partial H/\partial t$ and the assumption of constant velocity proportional to E_{ex} for the outgoing electron. The latter approximation overestimates t_0 at all energies and leads to $t_0 = \infty$ at $E_{\mathrm{ex}} = 0$. The system will, therefore, be closer to the sudden limit than is indicated by Eq. (4), especially at low energies. It would be reasonably straightforward to use a semiclassical treatment of this problem, in which the motion of the ejected electron through the valence shell and away from the ionized atom is treated classically and the excitation of the atom is treated quantum mechanically. Such an approach would be free of the major approximations that have been made here, but would lose sight of the simple dependence of the adiabaticity on ΔE and E_{ex}.

The discussion presented here deals only with that part of the satellite structure that can legiti-

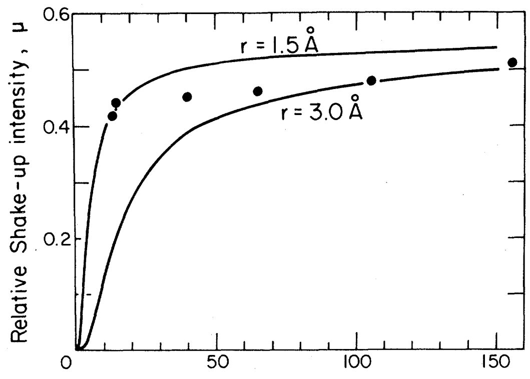

FIG. 1. Relative shakeup intensity as a function of energy above the core-ionization threshold. Solid points, data for N_2 adsorbed on nickel from Ref. 1. Curves, calculated with Eq. (4) with $r = 1.5$ and 3.0 Å, respectively.

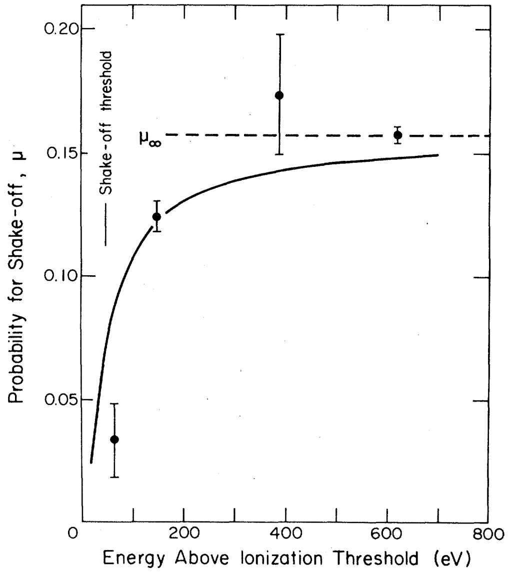

FIG. 2. Relative shakeoff intensity for neon as a function of energy above the core-ionization threshold. Solid points, data from Ref. 2. Curve, calculated with parameters described in text. The horizontal line labeled μ_∞ is the asympototic value for both the experimental data and the theoretical calculation.

mately be called shakeup or shakeoff, that is, the satellite strength that arises because the valence electrons rearrange in the presence of the newly formed core hole. In many cases, the same states can be reached directly by dipole transitions if configuration interaction is needed to describe either the initial or the final states. There may, therefore, be significant intensity to satellite states even in the adiabatic limit. This possibility was noted by Carlson and Krause.[2] The importance of initial- and final-state configuration interaction in the sudden limit has been investigated in detail by Martin, Mills, and Shirley.[11,12]

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