Double electron excitation in atomic Xe

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An x-ray-absorption experiment on atomic Xe shows a clear evidence of the electron shakeup (off) from the "valence" shells when an L-shell electron is excited. A Δ self-consistent-field (Δ SCF) calculation in the dipole approximation was performed based on a local-exchange potential and the sudden approximation. The experimental results show that the model is qualitatively and semiquantitatively correct. Double electron excitations exhaust almost all of the multielectron oscillation strength, which is about 20% of the total. The lowest-lying shake-up channel was found in the calculation to contain more than 70% of the total double excitation strength, which is a significant overestimate compared to the experiment. The energy dependence of the overlap integral S^2 in the Δ SCF approximation is presented. Finally, an effect is noted that depends on the symmetry of the initial state being excited and is not explained by the Δ SCF theory. There is a difference between the L_{I} and L_{II}, L_{III} edges in the change in slope of the absorption curve in passing through the three identified two-electron excitations. This suggests that there is a quantum interference between the one- and two-electron excitations not accounted for by the theory.

I. INTRODUCTION

One of the many-body effects noticeable in x-rayabsorption for atoms is that of multiple electron excitation, where, in addition to the usual direct electron excitation by the x ray, other electrons are excited through the Coulomb interaction between electrons. Multiple or double electron excitation here refers to both transitions to a final state with either bound or ionized electrons. It deserves special attention, since it occurs with significant strength, and it is a sensitive probe of the details of atomic structure and excitation dynamics.¹ With the use of currently available synchrotron radiation, x-rayabsorption has become a powerful tool for studying local atomic structure and electronic configuration in solids.² Although it is believed that many-electron effects may give a substantial reduction for the x-ray-absorption finestructure (XAFS) amplitude³ and may add features to the fine structure, they are generally ignored even close to the Several x-ray-absorption experiments edge region. claimed the identification of double electron excitation in solids.^{4,5} However, multielectron excitations in solids or molecules are very difficut to identify in general, especially for the excitation channels close to the absorption edge due to complicated electronic excitations and multiscattering effects. The many-electron excitation effects are not well understood presently and deserve both further theoretical and experimental investigations.

Experimental evidence of double electron excitation has been reported for several noble gas or closed-shell atoms, such as helium, beryllium, neon, argon, xenon, and krypton.⁶⁻¹⁵ The double electron excitation contributions to the total absorption were found to be significant, ranging from a few to several percent for helium⁷ to 40% near the beryllium 1s photoionization threshold.⁸ Theoretical calculations for double electron excitation or helium showed reasonable agreement with experiment if electron-electron correlations were included.^{16,17}

It is believed that the core rearrangement after oneelectron excitation is the main mechanism responsible for double electron excitation when the two electrons being excited are from different shells.^{1,18} The mechanism, known as the shake process, has been investigated by using the sudden approximation.⁷ This approximation was found to be poor near the excitation threshold, where the cross section of double excitation drops due to the dynamic screening of the nuclear charge by the low-energy photoelectron.¹⁹ An adiabatic to sudden transition is believed to occur in multielectron excitation.²⁰ In this picture, the cross section for the excitation of other electrons by the electron-electron interaction is gradually turned on as the excitation energy increases. However, it is not clear in what fashion and how high in energy the sudden limit will be reached. Other correlation effects also affect the multiexcitation satellite structure. Some of the effects are included in multiconfiguration shake theory^{21,22} and many-body perturbation theory.^{23,24}

We have performed an x-ray-absorption experiment on atomic Xe at the $L_{\rm I}$, $L_{\rm II}$, and $L_{\rm III}$ edges. The reason for choosing the L edges is because different symmetries are involved, which may produce different effects in the absorption process.²⁵ As discussed in the next section, double electron excitation satellites have been identified in the experimental spectra. A delta self-consistent-field (Δ SCF) calculation is presented in Sec. III for calculating the absorption spectra, and the results were compared with the experiment in Sec. IV. A brief preliminary report of this work has been given previously.²⁶

II. EXPERIMENT

The x-ray-absorption experiment was performed at Stanford Synchrotron Radiation Laboratory (SSRL) for the $L_{\rm I}$, $L_{\rm II}$, and $L_{\rm III}$ edges of Xe gas at room temperature under dedicated running conditions. To obtain data with

sufficient signal-to-noise ratio, it was necessary to minimize the harmonic content of the incoming beam. Harmonics introduce nonlinearities in the response of the ion chambers so that fluctuations in the incoming beam intensity are not cancelled when the ratio of the I_0 and Ichamber is taken, where I_0 is the semitransparent ion chamber before the sample monitoring the incoming intensity, and I is the ion chamber after the sample monitoring the transmitted intensity. The usual way of reducing harmonics by detuning the double-crystal monochromator was not sufficient for this case. The harmonic content of the beam at this low energy was so great that even after detuning, the residual harmonic content contributed sufficient nonlinearities to cause significant noise. It was necessary to further reduce the effect of harmonics by making the ion chamber semitransparent to the fundamental x-ray energy. In such a condition, the signal in the ion chamber per incident photon is approximately inversely proportional to the square of the photon energy. This is so because the absorption of a photon is approximately inversely proportional to the cube of the energy, and the signal contributed by an absorbed photon is proportional to its energy. Finally, to minimize distortion of



FIG. 1. (a) The experimental x-ray-absorption spectrum of the L_1 edge of Xe gas with a pre-edge background removed, plotted on an arbitrary scale. (b) An expanded scale of a portion of (a), showing the three two-electron excitation bumps and the change in slope occurring at the 85-eV bump indicated by an arrow.

the x-ray-absorption signal by any remaining harmonic contribution, the sample was made relatively thin²⁷ such that the absorption step $\Delta\mu\chi$ was less than 1.2 for all *L* edges. The absorption coefficient, for a few hundred eV above each absorption edge, was measured in a transmission mode with about 10⁹ photon counts per point statistic. Figs. 1–3 show the absorption coefficients for the $L_{\rm I}$, $L_{\rm II}$ and $L_{\rm III}$ edges, respectively, with a pre-edge background having been subtracted out.

A few features can be seen from the figures. As shown in part (a) of Figs. 1–3, the L_{II} and L_{III} spectra that are similar have sharp peaks at the threshold of absorption, but the spectrum for L_{I} is more like a step. In addition to the main peak, as shown in the expanded scale of the (b) portion of Figs. 1-3, all three spectra have some fine structure added on to the smooth curve above the edge; we can recognize three "bumps" for each spectrum at similar energies from the threshold. The slope of the spectrum changes at each bump for all three edges. The $L_{\rm I}$ edge shows a different behavior for the slope change, especially at the third bump indicated by the arrow. The slope beyond the third bump for the L_{I} edge increases, but decreases for $L_{\rm II}$ and $L_{\rm III}$. The positions of the bumps relative to the edge were determined by selecting the energy of the edge or bump to be one half of the step height, and the results are listed in Table I.



FIG. 2. Similar plots as in Fig. 1 but for the L_{II} edge.

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	Experiment (eV)	Theory (eV)	Cs binding energy (eV)	
p bump	12	12	11.4, 13.1 (5p)	
s bump	23	22	22.7 (5s)	
d bump	78	78	76.5, 78.8 (4 <i>d</i>)	

TABLE I. Bump positions for Xe L edges.

The ground state of Xe consists of 54 electrons filling the atomic orbitals from 1s to 5p. We estimate the multielectron transition from the Z + 1 rule, which states that the energy needed to eject a second electron in an outer shell of an atom with Z electrons, which has lost a deep core electron, is equal to the binding energy of the same shell of an atom with Z + 1 electrons. Some binding energies of Cs, the next element to Xe in the periodic table, are also listed in Table I. Comparing these energies with the energies of the bumps and noting that the three lowest occupied atomic shells for xenon are 5p, 5s, and 4d, we can recognize that the three bumps on each spectrum are the "satellites" corresponding to second electron excitations from these shells.



FIG. 3. Similar plots as in Fig. 1 but for the L_{III} edge.

III. Δ SCF CALCULATION

In order to understand the features of the spectra observed in the experiment, a calculation of the absorption spectra was performed. The calculation used the selfconsistent-field method and the sudden approximation. Each of the many electron wave functions used in this calculation was a single Slater determinant of Herman-Skillman (HS) atomic functions²⁸ with a given configuration. This program solves the nonrelativistic Hartree-Fock-Slater (HF) equation for each electron configuration.

Several approximations were made in this calculation. A spherical averaged central field approximation was first made to simplify the potential. Then the exchange potential was approximated by the free-electron exchange potential, e.g., the $X\alpha$ potential (the value α is a user specified input that is taken from the tabulation of Schwarz²⁹). As discussed by Herman and Skillman in Ref. 28, a modified potential V(r) is used in the calculation. The exchange should be replaced at large distance $r > r_0$ by the form

$$V(r) = -2(Z - n + 1)/r, \quad r > r_0 , \qquad (1)$$

where *n* is the number of electrons in the atom. The r_0 is the value of *r* at which the X_{α} potential equals V(r).

Many-electron wave function. The starting point of our calculation of the absorption coefficient is Fermi's golden rule, which can be written in the dipole approximation as

$$\sigma = 4\pi^2 \alpha (E_f - E_i) |M|^2 \rho(E_f) , \qquad (2)$$

where $M = \langle \Psi_i | \sum_j z_j | \Psi_f \rangle$ is the matrix element in the length form and $\alpha = e^2 / \hbar c$ is the fine-structure constant. The sudden approximation for the atomic potential was used, i.e., it is assumed that a sudden change of the selfconsistent potential occurs upon single or double excitations. The single electron orbitals for bound states in the atom were calculated using the HS program with one *L*shell electron missing for the final state of a one electron excitation and an additional electron missing for the final state of a double electron excitation. *L-S* coupling was used for the angular and spin part of the single electron orbitals.

The excited electron orbital in a continuum energy state was calculated using the radial Schrödinger equation with the self-consistent atomic ground ionic state potential calculated by the HS program, for the state that has one *L*-shell hole in it for the one-electron excitation and one *L*-shell hole and one valence hole for the twoelectron excitation; for $r > r_0$, the potential used was the corresponding Coulomb potential of the ion [Eq. (1)]. The program then integrates the Schrödinger equation to an R ($R > r_0$) and matches the solution to a free-space Bessel function solution. Several *R*'s were used to test the results, and it was found that for R > 80 bohr, the results converged for the wave function inside of the atom.

This continuum-orbit calculation ignored all correlations between the photoelectrons and electrons in the atom except those accounted for by the average ionic potential acting on the photoelectron. The excited electron orbit for two electrons in the continuum energy states were obtained independently for each of them using the same potential with one core hole and one valence hole. In so doing, we ignore the correlation or interactions between the excited electrons. The Slater determinants were then formed from the atomic or excited orbitals to represent initial or final states of the quantum systems, respectively. Note that the ground state and excited states are not strictly orthogonal to one another because they sense different average potentials.

Frozen deep core approximation. A frozen deep core approximation was used to simplify the large dimension Slater determinant, i.e., the three outermost shells in the Xe atom, namely, 4d, 5s, and 5p, were separated from the deep core and regarded as the "valence shells." Physically, the atomic potential in the core region does not change much after a deep core electron excitation because the screening of other electrons is weak. The deep core senses almost the full nuclear potential, and changing the screening by one electron will be a change of the order 1/Z. Therefore, the deep core overlap is very close to unity. A core state was included in the wave function only when it was excited in the absorption of an x-ray photon; otherwise, the core shell was treated as "frozen" in the transition. Since the overlap integral is equal to unity for the same shell before and after excitation and zero for different shells, the core shell that was not involved in the transition was dropped from the wave function. For example, 2s, 4d, 5s, and 5p states were the only ones included in the initial state for the L_{I} edge calculation.

The error in the frozen core approximation can be estimated as follows. The core orbital that is not involved in the direct x-ray-absorption is involved in the matrix element calculation from the determinant wave function in two ways. One is from the overlap with itself before and after the excitation, and other one is the replacement term that replaces the direct transition orbit and overlaps with an excited orbital if they have the same L-S symmetry. The core level that will give the larger contribution is the one least tightly bound, namely, the 4p states. We therefore estimate the error in the frozen core approximation for this worst case. For the transition from 2s to 6p, the matrix element will include the following terms if only the 2s, 4p, 5p, and 6p states are considered (where 4p is a core state): (A) Direct transition: $\langle 2s|r|6p'\rangle\langle 5p|5p'\rangle\langle 4p|4p'\rangle$, (B) Valence replacement:

 $\langle 2s|r|6p'\rangle\langle 5p|5p'\rangle\langle 4p|4p'\rangle$, (B) Valence replacement: $\langle 2s|r|5p'\rangle\langle 5p|6p'\rangle\langle 4p|4p'\rangle$, and (C) Core replacement: $\langle 2s|r|4p'\rangle\langle 5p|5p'\rangle\langle 4p|6p'\rangle$. It can be shown that the term (C) is much smaller than the term (B) from firstorder perturbation theory, in which the overlap of

$$|\langle \phi_1 | \phi_2' \rangle| \simeq \left| \frac{V_{12}}{E_1 - E_2'} \right| , \qquad (3)$$

where V_{12} is the matrix element of the change in potential, E_1 is the energy of the initial state ϕ_1 , and E'_2 is the energy for the excited state ϕ'_2 . Since the energy difference between 5p and 6p orbitals is much smaller than the difference between 4p and 6p orbitals, the (B) term is much larger than the (C) term. Therefore the (C) term can be ignored. The overlaps for valence and core shells have been calculated by using the HS program. The overlap for the 5p state, $\langle 5p | 5p' \rangle$, in the oneelectron excitation was 0.969, for the 5s state 0.988, for the 4d state 0.996, and all the overlaps in the core states were larger than 0.999. So the $\langle 4p | 4p' \rangle$ overlap integral can be approximated by unity.

Matrix element. The Slater determinants of initial and final states for the different channels of transitions were then formed. The matrix element calculations are straightforward, and the result for the single electron excitation of the L_1 edge $(2s \cdot \epsilon p)$ is

$$M_{\epsilon} = [\langle \epsilon p^{+} | z | 2s \rangle \langle 5p^{+} | 5p \rangle^{6} - \langle 5p^{+} | z | 2s \rangle \langle \epsilon p^{+} | 5p \rangle \langle 5p^{+} | 5p \rangle^{5}] \times \langle 5s^{+} | 5s \rangle^{2} \langle 4d^{+} | 4d \rangle^{10}, \qquad (4)$$

where ϵp is a continuum state with *p*-symmetry. The + sign by the wave function indicates it is calculated for the excited atomic potential with a single core hole. The second term in the parentheses is a replacement term. The summation is done among different symmetries. For the $L_{\rm II}$ and $L_{\rm III}$ edges, in addition to the direct transition from 2*p* to ϵd and ϵs states, the replacements are between 4*d* and ϵd and between 5*s* and ϵs , respectively. The results are similar for excitations to discrete states. The result for the transition of one electron from 2*s* to $\epsilon_1 p$ states and another one from 5*p* to $\epsilon_2 p$ states is given as follows:

$$M(2s - \epsilon_{1}p, 5p - \epsilon_{2}p) = [5(\langle \epsilon_{1}p^{++}|z|2s \rangle \langle \epsilon_{2}p^{++}|5p \rangle \langle 5p^{++}|5p \rangle^{5} - \langle 5p^{++}|z|2s \rangle \langle \epsilon_{1}p^{++}|5p \rangle \langle \epsilon_{2}p^{++}|5p \rangle \langle 5p^{++}|5p \rangle^{4})^{2} + (\langle \epsilon_{1}p^{++}|z|2s \rangle \langle \epsilon_{2}p^{++}|5p \rangle \langle 5p^{++}|5p \rangle^{5} - \langle \epsilon_{2}p^{++}|z|2s \rangle \langle \epsilon_{1}p^{++}|5p \rangle \langle 5p^{++}|5p \rangle^{5})^{2}]S^{2}_{4d,5s}.$$

(5)

Here the different shake-up channels have been summed up. The "++" sign by the wave function indicates it is calculated for the excited atomic potential with a single core hole and a valence hole (in this case a 5p hole). The symbol $S_{4d,5s}^2$ denotes all the 5s and 4d overlap integrals. All the matrix elements for other edges and other excitation channels have similar expressions. In the calculations of matrix elements, the angular and spin parts of the wave functions were first integrated analytically. It was found that the matrix elements for the L_{II} and L_{III} edges are the same except for a factor of 2 difference due to the different degeneracies. In the absorption crosssection calculation, the free-electron density of states was used for the density of final states when the excited electron ends up in a continuum state. An integration has to be carried out for the matrix element for two electrons excited to continuum energy states, since both electrons can have any distribution of kinetic energy consistent with the total energy being conserved. The cross section in atomic units can be written as

$$\sigma = 4\pi^2 \alpha (E_f - E_i) |M|^2 , \qquad (6)$$

where

$$M^{2}(E) = \int k_{1}^{2} dk_{1} \int k_{2}^{2} dk_{2} \delta(E - \epsilon_{1} - \epsilon_{2}) |M_{\epsilon_{1}, \epsilon_{2}}|$$

=
$$\int_{0}^{E} d\epsilon \sqrt{2\epsilon(2E - 2\epsilon)} |M_{\epsilon, E - \epsilon}|^{2}.$$

IV. RESULTS AND DISCUSSION

Single electron excitation spectrum. The single electron excitation spectra were calculated to 20 Ry above the edge with the Δ SCF approximations made in the last section. The results are shown in Fig. 4 by the lowest curve of points. Figure 4(a) is for the L_{I} edge and 4(b) for the $L_{\rm II}$ edge. The $L_{\rm III}$ edge is the same as the $L_{\rm II}$ edge but twice as large. In these figures the transitions to the discrete states just below the continuum edge (at zero eV) were omitted, since the energy width for these excited states is unknown from the calculation. These transitions will be added later with widths obtained from experiment. For comparison, a non-self-consistent-field (NSCF) calculation was made in which the initial potential was used to obtain the final state and only one electron excitation was allowed. The results are plotted in Fig. 4 for the two edges as the dashed line.

A comparison can be made between the single electron excitation spectrum in the Δ SCF model and the spectrum in the non self-consistent approximation model, where the final states remain the same as the initial HF states. Both curves are smooth except that the NSCF one for the $L_{\rm I}$ edge shows a minimum close to the edge that is absent for the Δ SCF one. Both spectra have about equal strength right at the $L_{\rm I}$ edge and separate from each other when moving away from the edge reaching a constant separation asymptotically. It is similar for the $L_{\rm II}$ edge except that the NSCF curve remains higher even at the threshold with a smaller separation compared to the region away from the edge. The overall strength of the NSCF calculation is more than 20% larger than the Δ SCF calculation. Since the NSCF model allows only one-electron excitations, the strength of the single excitation in this model represents the total strength in the xray-absorption process. The strength of the single excitation in the Δ SCF model however, is not the total strength since multielectron excitations are left out.

Double electron excitation spectrum. They are three types of final states for double electron excitations depending on discrete or continuum states. They are (i) two electrons excited to bound states, (ii) one to discrete, one to continuum states, and (iii) both electrons excited to continuum states. The former two types are called electron shakeup and the third, electron shakeoff. The cross sections of all the three types of excitation were calculated with the discrete states being included up to n=9. The contribution of the remainder can be approximated by the n^{-3} rule,¹⁷ which states that the product of n^3 with the square of the transition matrix element to excited state n, is a constant as $n \rightarrow \infty$. This rule has been tested for the Hartree-Fock states for L_1 absorption. We took n=2 for the transition of 2s to 6p, since it is the



FIG. 4. (a) The x-ray-absorption cross section σ for the $L_{\rm I}$ edge of Xe atoms for transitions to the continuum. The points show the values for single electron excitations in the Δ SCF approximation, while the dashed curve is the result for the non-self-consistent approximation (NSCF) where the final states remain the same as the initial HF states. The solid curve is the sum of the one- and two-electron excitation in the Δ SCF approximation. The excitation of both electrons to discrete states are not included. (b) Same as in (a) except for the $L_{\rm II}$ edge.

lowest-lying excitation channel. The constant is 5.4 for 2s to 6p, 7.0 for 2s to 7p, 8.0 for 2s to 8p, and 8.3 for 2s to 9p indicating convergence to about 8.5. Thus, the remaining strength can be estimated by the integral as

$$M_{\rm rem} = 8.5 \int_{N+1}^{\infty} \frac{1}{n^3} dn = \frac{8.5}{2(N+1)^2} , \qquad (7)$$

where N is the highest excited state included.

The cross sections for the L_1 edge with one electron in a continuum state and the second electron in 6p, 6s, and 5d states are shown in Fig. 5. The cross sections for excited-to-higher-energy discrete states are similar but several-fold lower in strength. All the cross sections show an increase near the energy threshold and decrease smoothly as the energy increases. The cross section of the 5p-6p shake-up channel is much larger than the *s*-s or *d*-*d* shakeup's, giving about 15% of the strength to the total cross section. The results for the L_{II} edge are somewhat similar to the L_{I} edge, with a different scale.

The cross sections for the continuum shake-off channel are plotted in Fig. 6 for the d,s, and p shake-off transition channels of the L_{II} edge. The shape of the cross section, which is zero at the energy threshold and increases to an asymptotic value, is opposite to that of the shake-up channel and is due to the integration of the matrix element in Eq. (6). The strengths for the three cross sections do not differ dramatically, which makes the shake-off channel more important in the case of s and d bumps.

The double electron excitation energy threshold can be determined in the one-electron picture as

$$\varepsilon = \varepsilon_f^{++} - \varepsilon_i^+ , \qquad (8)$$

where ε_i^+ and ε_f^{++} are the energies for the initial and final states of a monopole transition (shakeup and shakeoff) in the HF picture. The shake-off and shake-up channels that were calculated up to 9p, 9s, and 8d are



FIG. 5. The x-ray-absorption cross sections for various double excitation channels of L_1 edge shakeup with the other electron in the continuum state with p symmetry. The shakeup 5p to 6p (solid), 5s to 6s (dashed), and 4d to 5d (dotted) are shown. Note that the zero threshold is set to the same value of 0 eV even though their absolute values differ as given in Table I.



FIG. 6. Similar to Fig. 5, except that shake-off channels are calculated for both final electrons are in continuum states.

added to the single electron excitation spectrum starting at the double excitation thresholds. These one- plus-two electron excitation cross sections are shown in Fig. 4(a) for the $L_{\rm I}$ edge and Fig. 4(b) for the $L_{\rm II}$ edge in solid lines. Again, the discrete excitation channels are missing in these figures.

Comparison can be made in Fig. 4 between single plus double electron excitation in the Δ SCF picture and the single excitation in the NSCF picture. The agreement is within a few percent for both L_{I} and L_{II} edges over the whole spectra except at the threshold of the p bump. The missing excitation strength for one-electron excitations in the Δ SCF picture compared to the NSCF calculation is found mainly in the double electron excitations. The cross section for double excitation is about 20% of the total cross section over the spectra, and more than 80% of the double excitation cross section is contributed by the shakeup of the electrons in the outermost valence shell 5p to the lowest excited state having the same symmetry, 6p. In Table II, the cross sections for different edges at 4 Ry from the edge are listed along with the tabulated and calculated values, which were linearly interpolated from Refs. 30 and 31. The sum of the cross sections for single and double electron excitations from Δ SCF is in good agreement with the cross sections calculated from NSCF. The agreement between our calculation and the tabula-tion of McMaster, *et al.*³⁰ is good to within several percent. Our Δ SCF cross sections are larger than the calculated cross section compiled by Saloman and Hubbell.³¹ However, the comparison made is not over the whole spectrum but only for near the edge step.

Comparison with experiment. It is reasonable to define the energy threshold for double excitation as the energy needed for shakeup to the lowest-lying excited states. The energy thresholds were calculated according to Eq. (8) and are listed in Table I for the $L_{\rm I}$ edge. These results agree very well with the energy thresholds from the xenon experiment, and similar agreements were found for the $L_{\rm II}$ edge.

It is difficult to compare the double electron excitation cross section between the calculation and the experiment

TABLE II. Calculated cross section at an energy of 4 Ry past the edge steps, compared with other results. All cross sections in units of 10^{-19} cm².

Edges	ΔSCF_1^a	ΔSCF_2^{b}	NSCF°	McMaster et al. ^d	Saloman et al. ^e
L_{I}	0.23	0.28	0.28	0.26	0.23
	0.44	0.55	0.55	0.54	0.46
	0.89	1.09	1.09	1.02	0.98

^aCross sections for single-electron excitation.

^bSum of cross sections for single and double electron excitations.

^cCross sections for non-self-consistent calculation.

^dReference 29.

^eReference 30.

for the satellite near the edge because the double excitation cross section is not separable there from the total cross section in the experiment. However, for the satellite far from the edge, the prebump background is smooth and can be subtracted out to obtain the strength for the bump. The ratio between this bump and the total experimental absorption is about 0.8%, compared to about 1.0% from the calculation.

To compare the calculated spectrum with the experiment, the excitations to discrete states should be included for both single and double excitations. Table III shows the cross sections for single discrete transitions up to n=9 for both edges. The program cannot handle the calculation of higher discrete states due to convergence problems; also it is not reliable from a theoretical point of view, since the HF equation is correct only for the ground state and low-lying excited states. The cross sections for two-electron discrete transitions were also calculated. The remaining strength for the states of n larger than 9 is estimated by the n^{-3} rule [Eq. (7)]. A Gaussian width is assumed for the edges and the bumps, which is given in the normalized form as

$$\rho(\epsilon) = \left[\frac{\ln 2}{\pi}\right]^{1/2} \frac{1}{\Delta \epsilon} \exp\left[-(\ln 2)\left[\frac{\epsilon}{\Delta \epsilon}\right]^2\right],$$

where ϵ is the energy from the threshold and $\Delta \epsilon$ is the half width of an edge or a bump. These cross sections

TABLE III. Integrated cross section σ_{I} to discrete states in units of 10^{20} cm² Ryd.

$L_{\rm I}$ edge		$L_{\rm II}$ e	edge
Fillal State		Fillal state	
n,l	σ_{I}	n, l	σ_{I}
6,1	0.6724	5,2	0.9075
7,1	0.2610	6,2	0.5718
8,1	0.1255	7,2	0.1639
9,1	0.0660	8,2	0.0766
		9,2	0.0322
		6,0	0.0382
		7,0	0.0138

were then added for different edges and bumps according to the energy threshold given from the calculation of Eqs. (7) and (8), and convoluted with the Gaussian distribution. The energy width of the main edge can be found in Ref. 32, but the width for the double excitation bump was not known, and a larger width was chosen to show agreement with the measurements. The main peak width is 3.5 eV for the $L_{\rm I}$ edge and 2.3 eV for the $L_{\rm II}$ edge from Ref. 32. The double excitation bump width is estimated by comparing the d bump (4d electron shakeup and shakeoff) width with the width of the main absorption peak from the experiment. It is found that the double bump width is 60% larger than the single excitation width. Therefore, the shake-up (-off) bump width used is 5.6 eV for the L_{I} edge and 4.0 eV for the L_{II} edge. The results are shown in Figs. 7(a) and 7(b) for the L_{I} and L_{II} edges, respectively. The results of the NSCF model including the lifetime broadening are also shown in the same figures.

The spectra in Fig. 7 can be compared with the experiment shown in Figs. 1-3. Qualitatively, the calculation and the experiment are similar in the sense that there are double electron excitation satellites besides the main absorption edge. Quantitatively, good agreement was found for the location of the bump and for the relative strength of the d bump as showed previously. Poor agreement near the absorption edge is apparent. The calculation exaggerates the double excitation cross section for the pbump making the two spectra dissimilar near the edge. The d double excitation cross section calculation appears to agree with the experiment. It is, however, clear that in order to get agreement between experiment and theory, multielectron excitation should be included. The Δ SCF calculation does show a significant improvement over the NSCF single electron model along the whole spectrum.

One interesting difference between the Δ SCF calculation and the experiment is shown in part (b) of Figs. 1–3. The experiment has a change in slope at the two-electron excitation thresholds that depends on the symmetry of the core electron being excited. For example, the $L_{\rm I}$ edge, which has a core electron of s symmetry, shows an increase in slope at the arrow, while the $L_{\rm II}$ and $L_{\rm III}$ edges, which have core electrons of p symmetry, show a decrease in slope at the arrow. The calculation predicts an increase in slope and thus can explain qualitatively



FIG. 7. Calculated x-ray-absorption cross section for the $L_{\rm I}$ (a) and $L_{\rm II}$ (b) edge of Xe atoms. The Δ SCF calculation including all single and double electron excitations with lifetime broadening is shown by the solid line. The dashed line is the NSCF calculation with lifetime broadening.

only the $L_{\rm I}$ edge. The decrease in slope observed in the $L_{\rm II}$ and $L_{\rm III}$ edges suggests that the multielectron and single electron excitation cross section cannot be simply added together as this addition increases the slope according to our Δ SCF calculation. The decrease can be understood if some portion of the matrix elements for the two processes need to be added together before squaring, allowing the possibility of an interference between the two.

For the $L_{\rm I}$ edge, the single electron excited has p symmetry, while for the two-electron excitation, one has p symmetry and the other has d symmetry for the threshold at the arrow in Fig. 1. For the $L_{\rm II}$ and $L_{\rm III}$ edges the dominant absorption has corresponding symmetries of d, and d plus d. The Δ SCF calculation does not allow for any interference between the single electron and two-electron matrix elements because it is assumed that these are two distinguishable final states. The experimental results suggest that this assumption is in error for the $L_{\rm II}$ and $L_{\rm III}$ edges.

There is a subtle effect in the Δ SCF calculation that causes a small interference effect between the one- and two-electron excitations. The final states of the single and double excitations are not exactly orthogonal to one

another because the atomic potentials are different in the two cases. We neglected this effect as is usually done in the Δ SCF calculation. A unitary transformation could be made on the wave function making them orthogonal to one another.²⁵ The error of this neglect would be slightly greater for the 4d electron shakeup (off) for the $L_{\rm II}$ and $L_{\rm III}$ edges than for the $L_{\rm I}$ edge, since all the final states have d symmetry in the formal edge. The experiment may indicate that such subtle effects should be included to explain the change in slope past a multiexcitation threshold. We made an estimate of the correction introduced by the nonorthogonality between the single and double excitations. Our preliminary estimation was too small to explain the experiments.

The overestimate of the two-electron excitations close to the edge is presumably the result of the sudden approximation in the Hartree-Fock picture, in which noninteracting electron states are assumed, and all the extrinsic and dynamic effects between photoelectron and the other electrons are ignored when the excitation occurs. The extrinsic effect tends to reduce the strength of double electron excitation.³³ The x-ray-absorption is a dynamical process in which the photoelectron experiences interactions with the nucleus and other electrons as it makes its transition out of the atom. Near the single electron excitation threshold, the interaction between a slow outgoing photoelectron and the other electrons may not be negligible, and treating this by a single HF configuration and the sudden approximation may be poor approximations. To improve the calculation would require including configuration interactions.

Relation to XAFS. In the discussion of many-electron effects in x-ray-absorption fine structure (XAFS),³ the "passive" electron contribution to the XAFS is approximated by a many-body overlap integral in the one-electron transition picture, namely,

$$S^{2} = |\langle \Psi_{f}^{N-1} | \Psi_{i}^{N-1} \rangle|^{2} , \qquad (9)$$

where Ψ^{N-1} is the total wave function for the N-1 passive electrons. In the high-energy limit, the overlap integral is a constant independent of the momentum or wave number of a photoelectron. This integral is about 0.78 for the $L_{\rm II}$ edge and 0.74 for the $L_{\rm II}$ edge in the xenon calculation.

In the Δ SCF picture, the S^2 term varies at lower energies due to the presence of replacement terms [see Eq. (4)]. Figure 8 shows this energy dependence at the *L* edge of Xe by plotting the ratio between the one-electron excitation cross sections in the Δ SCF model and the NSCF model for the L_I (solid) and L_{II} (dashed) edges with respect to photoelectron kinetic energy. Both curves show a smooth decrease with increase of energy from close to unity at the edge to the constant high-energy value. So the effect of the replacement terms is to increase S^2 . The S^2 term decreases to its high-energy value as the replacement terms go to zero at high energy.

It has been pointed out that multielectron shake-up satellites are present in the x-ray-absorption near-edge spectra of MnCl₂, FeCl₂ and CoCl₂.⁵ Our experiment and calculations indicate that other satellites occur in the



FIG. 8. The calculated S^2 as a function of energy past the edge for the L_1 (solid) and L_{11} (dashed) edges.

XAFS region such as the d bump found in xenon, although they are less visible due to their relatively small strength. In some highly disordered systems where the XAFS signal is weak, it is conceivable that the satellites may distort the XAFS. This possibility should be kept in mind.

The shake-up (-off) effect, besides directly producing a satellite structure in the absorption spectrum near the threshold, causes a more subtle effect.³ With a twoelectron excitation, the photon energy is shared between the two electrons. If the spread in energy for the second electron excitation is large, the multielectron excitations tend not to produce XAFS, since the kinetic energy for each electron can vary over a large range smearing out the oscillations.

The lowest-lying shake-up channel carries most of the strength for double excitations and almost 20% of the total absorption as indicated in the xenon calculation. Although, comparison with experiment indicates that this is an overestimate near the threshold of the shake-up channel, it is still possible that this channel contributes most of the multielectron oscillation strength. A theoretical calculation for an Ar K edge based on shake theory in its multiconfiguration form showed that shakeup is more important than shakeoff for outer shell excitations.³⁴ Since the shake-up channel has a small enough spread in energy, the outgoing part of the final state in x-ray-absorption can be approximated by a superposition of two Hankel functions for the K-edge absorption, one having the weight of the single particle excitation channel and the other of the lowest-lying shake-up channel, but displaced in energy by the shake-up threshold. The absorption coefficient can then be approximated as

$$\mu(E) = A_1 |M_1(k)|^2 (S_0^{N-1})^2 \rho(E_f) + A_2 |M_1(k_{nm})O_{nm}|^2 (S_0^{N-2})^2 \rho(E_f') , \qquad (10)$$

where

$$k_{nm} = [2(k^2/2 - \epsilon_{nm})]^{1/2}$$

is the wave number for the photoelectron when shakeup

occurs and ϵ_{nm} is the monopole transition energy for lowest-lying channel. Here O_{nm} is the monopole transition term from bound state *n* to bound state *m*. The EX-AFS (extended x-ray-absorption fine structure) formula now can be revised as follows by assuming $(S_0^{N-2})^2 = (S_0^{N-1})^2$ and the mean-free-path terms are equal to the two processes

$$\chi = \chi(k) + O_{nm} |^2 \chi(k_{nm}) , \qquad (11)$$

where $\chi(k)$ is the ordinary EXAFS. In the case of Xe, ϵ_{nm} is about 12 eV and k_{nm} shifts a significant amount from k. This will add a slightly slower varying EXAFS oscillation to the "main" EXAFS signal. This point has been discussed by Rehr et al.³ and the effect was estimated to be about 10% in Br₂.

V. CONCLUSION

An x-ray-absorption experiment shows clear evidence of the double electron monopole excitation from the 4d, 5s, and 5p valence shells of atomic Xe when an L-shell electron is excited. The bumps corresponding to each channel of monopole excitation have an edgelike shape increasing rapidly at the energy threshold for the excitation. A Δ SCF calculation of the absorption cross section in the dipole approximation was performed, which used a local exchange potential but did not include spin-orbit coupling or other relativistic corrections. The edge steps from the calculation for all the L edges agree rather well with measurement. The calculation of the location of each double excitation bump is in reasonable agreement with the experimental spectra. The calculated double excitation contribution is found to be about 20% of the total absorption cross section over the whole energy region, with the main contribution coming from the shake-up channel of the outermost shell. The comparison with experiment is poor for the lowest-lying double excitation near the edge; the calculated strength is too large. Better agreement is obtained for the higher-energy double excitations. The calculated step of the 4d bump at 80 eV from the edge agrees reasonably well with the experiment. The neglect of correlations among electrons in the Δ SCF approximation presumably can account for the disagreement. However, the calculation shows that the simple Δ SCF model used in this work is qualitatively and semiquantiatively correct.

A new phenomenon is noted from the experimental measurement at the double electron excitations, which is not explained by the Δ SCF calculation. The slope change after each excitation threshold of the 4d, 5s, and 5p valence shell depend on the symmetry of the initial core level being excited. The slope of the absorption spectrum at the third bump of L_1 edge increases with energy, where a 2s electron and a 4d electron are being excited, while the slope of the third bump decreases with energy for the $L_{\rm II}$ and $L_{\rm III}$ edges, where a 2p electron and a 4d electron are being excited suggesting an interference between the one- and two-electron excitation channels in the latter case.

The relation between this work and XAFS has been

discussed. The energy dependence of the S^2 overlap was found to be monotonically decreasing from the edge approaching a constant overlap integral. The satellite structure of multielectron excitations can be several percent of the total excitation and down to about 1% in XAFS region as shown in the x-ray-absorption experiment for Xe. It is suggested that corrections are needed for the XAFS if multiexcitations occur and the sample material is highly disordered.

The multiexcitation corrections for XAFS shown by this work are not simply accounted for by an overlap integral in the XAFS region. Due to the fact that the dominant part of the double excitations in the Xe calculation comes from one or two lowest-lying shake-up channels, the outgoing part of the final state is no longer a single Hankel function with wave number k but a superposition of Hankel functions with slightly different wave numbers. The effect would cause the XAFS signal for the two waves to be out of phase in the low-k region. In the EX-AFS region, the two waves tend to add to each other making the EXAFS signal stronger than reduced by the overlap integral.

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