# Calculation of Electron Shake-Off Probabilities as the Result of X-Ray Photoionization of the Rare Gases*

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The probability for either exciting or ionizing an electron from a given atomic orbital as the result of a sudden vacancy in one of the atomic shells, such as might occur with photoionization, has been calculated through the use of the sudden approximation. Calculations were made for each of the subshells of neon, argon, krypton, and xenon as a function of the location of the initial vacancy. The calculations were based on relativistic Hartree-Fock-Slater wave functions. The results were generalized in terms of the change in effective charge. For example, electron shake-off in the valence shell was found to be nearly independent of the location of the initial core vacancy, increasing slightly as one goes to the lower principal quantum numbers. The ionization potentials were also found to be nearly independent of the location of the core vacancy. The results of the electron-shake-off calculations were also used to obtain an evaluation of the relaxation energy arising from the promotion of a single vacancy, and compared with values obtained from binding-energy calculations. Results of the electron-shake-off calculations are applicable to any process that leads to a sudden creation of a vacancy in an atom. However, particular emphasis is given to photoelectron spectroscopy in discussing the results.

## I. INTRODUCTION

Photoejection of a shielding electron from the core of an atom results in a sudden change in the central potential as viewed by electrons in the outer shell of that atom. This sudden change in potential can excite other electrons in the atom from their ground-state orbitals into the continuum (electron shake off) or into discrete excited states (electron shake up). This possible source of multiple excitation is of importance to the general area of photoionization. In particular, the recent growth of interest in x-ray photoelectron spectroscopy has increased our need to understand electron shake off and shake up. Satellite lines are created in photoelectron spectra as the result of electron shake up. The intensities of the main lines in photoelectron spectra are dependent on the probability for electron shake off, and binding energies as obtained from photoelectron data can be related to calculated eigenvalues by means of Koopmans's theorem, if shake-off probabilities are known.[1,2]

In this paper we have calculated shake-off probabilities, based on the sudden approximation, using single-electron relativistic Hartree-Fock-Slater atomic wave functions.[3] Similar comprehensive calculations were previously made[4] on electron shake off as a consequence of $\beta$ decay. Calculations of electron shake off as a result of a given inner-shell vacancy (such as photoejection or electron impact ejection) have been reported for neon, argon,[5,6] and krypton.[7] Some electron shake-off calculations on the rare gases can also be found in an earlier report,[8] including the results of a 1$s$ hole in Xe. What we present here is a complete set of calculations for shake-off probabilities resulting from a hole in each of the subshells of neon, argon, krypton, and xenon. With this comprehensive set of calculations it is possible to generalize about behavior of electron shake off as a function of the initial vacancy. In addition, we have used the shake-off probabilities to help in estimating the relaxation (or reorganization) energies; and we have compared these values with those obtained from binding-energy calculations.

## II. THEORY

The calculations made in this paper are parallel to those made on electron shake off as the result of $\beta$ decay.[4] The reader is strongly advised to read that paper for further details and general background as to the nature of these calculations.

Based on the sudden approximation, which assumes an instantaneous change in the Hamiltonian, the probability for an electron initially represented by the wave function $\psi_i$ to be found in a given final state $\psi_f$ is

$$P_{i\to f} = \left| \int \psi_f^* \psi_i \, d\tau \right|^2 . \tag{1}$$

If the final state differs from the initial state by a change in central potential, an electron in orbital $\psi_{nlj}$ will not necessarily remain in that orbital but may find itself in a different orbital, the transition being governed by monopole selection rules. The operator in Eq. (1) is unity.

In a sense this approximation views the problem as a two-step process: (i) a sudden change in the central potential followed by (ii) the excitation of an orbital electron as the result of the change in potential. Physically, the excitation and ionization occur concurrently. In the high-energy limit it is hoped that Eq. (1) will approach the observed probabilities. This treatment also implicitly disregards quantum statistics and omits antisymmetrizing the final-state vector. It is hoped that again in the high-energy limit these assumptions will not create a significant error. Åberg[9] has formulated the photoelectron cross section for double ionization in the dipole approximation. By making two assumptions (a) that the final-state channels are decoupled from each other and from all channels that correspond to various bound states of the residual ion and (b) that the electron-electron interaction is negligible in the final state so that the final state is described by a symmetrized product of two Coulomb wave functions, he was able to show that in high-energy photon limit that the cross section would approach that obtained from the sudden approximation as given in Eq. (1). Justification for using the sudden approximation and its attendant assumptions comes from the good agreement between theory and experiment, as will be discussed later in this paper.

Calculation of electron shake off can be accomplished using single-electron wave functions from Hartree-Fock solutions of the neutral atom (initial state) and ion with a single-hole configuration (final state). Excited states of the ion are more difficult to obtain than the ground state. Thus, it is preferable to calculate the probability that an electron *will remain* in an orbital with the same quantum number. This probability when subtracted from unity yields the chance an electron *will be removed* from the orbital. The probability for removing one or more electrons from an orbital designated by $n, l, j$, where $n$ and $l$ are the principal and orbital angular-momentum quantum numbers and $j = l \pm \frac{1}{2}$, is given by

$$P_{nlj} = 1 - \left[ \left| \int \psi^*_{nlj}(A_0)\psi_{nlj}(A)\,dr \right|^2 \right]^N - P_F , \qquad (2)$$

where $\psi_{nlj}(A)$ represents the orbital $nlj$ in the neutral atom and $\psi_{nlj}(A_0)$ represents the orbital $nlj$ in the ion $A_0$ whereby a single vacancy has been created in a given subshell of atom $A$. $N$ is the number of electrons in orbital $nlj$.

The quantity $P_F$ is a correction which arises from the condition that electron-shake-up transitions to occupied levels are not physically allowed. The correction for contributions to filled states (from $n' = 1$ to $x$) is[10]

$$P_F = \sum_{n'=1}^{n'=x} N \frac{N'}{2j+1} \left| \int \psi^*_{n'lj}(A_0)\psi_{nlj}(A)\,dr \right|^2 , \qquad (3)$$

where $n' \neq n$, and $N'$ is the number of electrons in the orbital designated by $n'lj$.

The single-electron radial wave functions used in Eq. (2) have been obtained from a relativistic Hartree-Fock-Slater solution of the atom and appropriate singly charged ions. The code used to obtain these solutions has been previously discussed.[3] Full Slater exchange was used.

## III. RESULTS AND DISCUSSION

### A. Electron Shake-Off Probabilities

The probability $P_{nlj}$ that at least one electron will be removed from a given orbital by means of electron shake off or shake up is given in Tables I–IV as a function of sudden creation of a hole in one of the subshells of neon, argon, krypton, or xenon. The probabilities are given in percent and include all the electrons in a given orbital. In Table V the results for removing a $1s$ electron from Kr are compared with a similar calculation using nonrelativistic Hartree-Fock wave functions. The conclusions reached in such comparisons is that though the results are of course dependent on the nature of the wave functions used, they are generally not highly sensitive to the wave functions.

Before discussing the results of the calculations, let us briefly review the limits of calculations based on the sudden approximation as illustrated by comparison with experiment. Numerous data have been taken with regard to electron shake off as the result of $\beta^-$ decay both for the inner-most $K$ or $L$ shells[11] and for the valence shell.[12] In general, calculations based on the sudden approximation have given reasonably good agreement with experiment as long as one dealt with processes within the region of the sudden approximation, which in the case of $\beta^-$ decay implies that the $\beta^-$ energy $\gg$ the atomic binding energy. During the last few years there has been extensive work done on more sophisticated approaches[11] to autoioniza-

TABLE I. Probability for electron shake off (%) for the various subshells in neon, $n_s$, as the result of a sudden vacancy in orbital, $n_0$.

| $n_0$ \ $n_s$ | $1s$ | $2s$ | $2p_{1/2}$ | $2p_{3/2}$ | $\Sigma P$ | $E_S$[a] | $E_R$[b] | $E_R/E_S$ |
|---|---|---|---|---|---|---|---|---|
| $1s$ | 0.030 | 1.71 | 5.44 | 10.63 | 17.8 | 15.9 | 24.8 | 1.56 |
| $2s$ | 0.000 | 0.16 | 1.48 | 2.98 | 4.6 | 3.4 | 4.8 | 1.42 |
| $2p_{1/2}$ | 0.000 | 0.34 | 0.78 | 3.14 | 4.3 | 3.2 | 4.7 | 1.47 |
| $2p_{3/2}$ | 0.000 | 0.34 | 1.55 | 2.35 | 4.3 | 3.2 | 4.7 | 1.47 |

[a] Average electron shake-off energy given by Eq. (5).
[b] Relaxation energy from Ref. 22.

TABLE II. Probability for electron shake off (%) for the various subshells in argon, $n_s$, as the result of a sudden vacancy in orbital, $n_0$.

| $n_0$ \ $n_s$ | $1s$ | $2s$ | $2p_{1/2}$ | $2p_{3/2}$ | $3s$ | $3p_{1/2}$ | $3p_{3/2}$ | $\Sigma P$ | $E_S$ [a] | $E_R$ [b] | $E_R/E_S$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $1s$ | 0.001 | 0.30 | 0.54 | 1.07 | 2.47 | 5.86 | 11.45 | 21.7 | 22.5 | 31.8 | 1.41 |
| $2s$ | 0.000 | 0.017 | 0.056 | 0.11 | 1.66 | 4.18 | 8.33 | 14.3 | 9.1 | 9.9 | 1.09 |
| $2p_{1/2}$ | 0.000 | 0.049 | 0.043 | 0.17 | 1.73 | 4.41 | 8.71 | 15.1 | 9.9 | 11.1 | 1.12 |
| $2p_{3/2}$ | 0.000 | 0.05 | 0.08 | 0.13 | 1.73 | 4.37 | 8.72 | 15.0 | 9.9 | 11.1 | 1.12 |
| $3s$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.16 | 1.37 | 2.82 | 4.4 | 2.2 | 1.8 | 0.82 |
| $3p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.25 | 0.57 | 2.33 | 3.2 | 1.6 | 1.4 | 0.88 |
| $3p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.25 | 1.12 | 1.74 | 3.1 | 1.6 | 1.4 | 0.88 |

[a] Average electron shake-off energy given by Eq. (5).
[b] Relaxation energy from Ref. 22.

tion in $\beta$ decay, in which the energy shared by the neutrino $\beta^-$ particle and shake-off electrons are considered as a single process. These calculations appear to give somewhat better agreement with experiment than those based on the sudden approximation, even in the region where the sudden approximation should apply. Nevertheless, the sudden approximation gives a reasonably good first estimate of electron shake off on which experiment and other theory can be tested.

With regard to photoionization it has been observed[5b] that the probability of $L$-shell electron shake off in neon as the result of $K$-shell photoionization is independent of the photon energy from about 300 eV to 17 keV, which is in agreement with the predictions of the sudden approximation. In addition the calculated shake-off probability is in agreement with the measured autoionization. Furthermore, x-ray and Auger satellite lines due to $KL$ double ionization arising from electron impact and photoionization have given good agreement with calculations[9] using the sudden approximation. For example, the simultaneous formation of $K$ and $L$ vacancies measured from x-ray satellites are compared by Åberg[9] with calculations based on the sudden approximation for elements from $Z=5$–36. The agreement is very good. Comparison between the calculated results of Åberg and the calculations reported in this paper on the probability for shake off in the $L$ shell of Ne, Ar, and Kr as the result of a $1s$ vacancy also shows excellent agreement. Also, calculations using the sudden approximation have been made for electron shake up into the $2s^2$, $2p^5$, $3p\,^1P$ state of neon as the consequence of photoionization in the $K$ shell and been confirmed by experiment.[13] Thus, there exists substantial experimental evidence that the sudden approximation gives good estimates for shake-off and shake-up probabilities as the result of photoionization as

TABLE III. Probability for electron shake off (%) for the various subshells in krypton, $n_s$, as the result of a sudden vacancy in orbital, $n_0$.

| $n_0$ \ $n_s$ | $1s$ | $2s$ | $2p_{1/2}$ | $2p_{3/2}$ | $3s$ | $3p_{1/2}$ | $3p_{3/2}$ | $3d_{3/2}$ | $3d_{5/2}$ | $4s$ | $4p_{1/2}$ | $4p_{3/2}$ | $\Sigma P$ | $E_S$ [a] | $E_R$ [b] | $E_R/E_S$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $1s$ | 0.002 | 0.060 | 0.089 | 0.18 | 0.22 | 0.38 | 0.75 | 1.43 | 2.13 | 1.80 | 4.39 | 9.06 | 20.5 | 33.4 | 53.6 | 1.60 |
| $2s$ | 0.000 | 0.002 | 0.007 | 0.014 | 0.89 | 0.15 | 0.31 | 1.36 | 2.04 | 1.50 | 3.78 | 7.97 | 17.2 | 17.7 | 26.1 | 1.47 |
| $2p_{1/2}$ | 0.000 | 0.008 | 0.006 | 0.026 | 0.099 | 0.18 | 0.36 | 1.42 | 2.14 | 1.53 | 3.86 | 8.13 | 17.8 | 19.2 | 29.1 | 1.51 |
| $2p_{3/2}$ | 0.000 | 0.008 | 0.011 | 0.018 | 0.097 | 0.17 | 0.36 | 1.41 | 2.12 | 1.52 | 3.84 | 8.10 | 17.7 | 19.3 | 28.6 | 1.48 |
| $3s$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.006 | 0.020 | 0.045 | 0.32 | 0.50 | 1.22 | 3.26 | 6.97 | 12.3 | 7.8 | 8.7 | 1.12 |
| $3p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.012 | 0.010 | 0.048 | 0.33 | 0.51 | 1.21 | 3.26 | 6.96 | 12.3 | 7.8 | 9.0 | 1.15 |
| $3p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.011 | 0.020 | 0.034 | 0.31 | 0.48 | 1.20 | 3.24 | 6.94 | 12.2 | 7.7 | 8.7 | 1.13 |
| $3d_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.012 | 0.023 | 0.050 | 0.27 | 0.55 | 1.19 | 3.22 | 6.88 | 12.2 | 7.8 | 9.1 | 1.17 |
| $3d_{5/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.012 | 0.022 | 0.049 | 0.35 | 0.45 | 1.18 | 3.21 | 6.87 | 12.1 | 7.7 | 9.0 | 1.17 |
| $4s$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.004 | 0.14 | 1.33 | 3.02 | 4.5 | 2.0 | 1.7 | 0.85 |
| $4p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | 0.20 | 0.50 | 2.31 | 3.0 | 1.4 | 1.3 | 0.93 |
| $4p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.18 | 0.96 | 1.66 | 2.8 | 1.3 | 1.2 | 0.92 |

[a] Average electron shake-off energy given by Eq. (5). [b] Relaxation energy from Ref. 23.

TABLE IV. Probability for electron shake off (%) for the various subshells in xenon, $n_s$, as the result of a sudden vacancy in orbital, $n_0$.

| $n_0$ \ $n_s$ | 1s | 2s | $2p_{1/2}$ | $2p_{3/2}$ | 3s | $3p_{1/2}$ | $3p_{3/2}$ | $3d_{3/2}$ | $3d_{5/2}$ | 4s | $4p_{1/2}$ | $4p_{3/2}$ | $4d_{3/2}$ | $4d_{5/2}$ | 5s | $5p_{1/2}$ | $5p_{3/2}$ | $\Sigma P$ | $E_S$ [a] | $E_R$ [b] | $E_R/E_S$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 0.001 | 0.023 | 0.032 | 0.061 | 0.073 | 0.11 | 0.22 | 0.22 | 0.32 | 0.23 | 0.37 | 0.73 | 1.65 | 2.46 | 1.67 | 3.73 | 8.39 | 20.3 | 43.6 | 66.9 | 1.53 |
| 2s | 0.000 | 0.001 | 0.002 | 0.005 | 0.028 | 0.038 | 0.082 | 0.16 | 0.24 | 0.14 | 0.22 | 0.46 | 1.63 | 2.46 | 1.48 | 3.36 | 7.76 | 18.1 | 23.7 | 34.8 | 1.46 |
| $2p_{1/2}$ | 0.000 | 0.003 | 0.002 | 0.009 | 0.032 | 0.052 | 0.10 | 0.18 | 0.27 | 0.15 | 0.24 | 0.50 | 1.67 | 2.51 | 1.50 | 3.41 | 7.86 | 18.5 | 26.2 | 38.9 | 1.48 |
| $2p_{3/2}$ | 0.000 | 0.003 | 0.003 | 0.006 | 0.030 | 0.045 | 0.099 | 0.17 | 0.26 | 0.15 | 0.23 | 0.48 | 1.66 | 2.50 | 1.49 | 3.39 | 7.83 | 18.3 | 25.4 | 37.5 | 1.48 |
| 3s | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.004 | 0.009 | 0.017 | 0.027 | 0.075 | 0.11 | 0.25 | 1.05 | 1.62 | 1.36 | 3.12 | 7.31 | 15.0 | 11.7 | 14.7 | 1.26 |
| $3p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.002 | 0.011 | 0.020 | 0.032 | 0.075 | 0.12 | 0.26 | 1.08 | 1.66 | 1.36 | 3.14 | 7.33 | 15.1 | 12.1 | 15.2 | 1.26 |
| $3p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.004 | 0.007 | 0.017 | 0.028 | 0.072 | 0.11 | 0.25 | 1.05 | 1.61 | 1.36 | 3.12 | 7.31 | 14.9 | 11.7 | | |
| $3d_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.005 | 0.014 | 0.023 | 0.047 | 0.079 | 0.12 | 0.27 | 1.15 | 1.75 | 1.37 | 3.15 | 7.35 | 15.3 | 12.8 | 16.3 | 1.27 |
| $3d_{5/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.006 | 0.013 | 0.028 | 0.037 | 0.078 | 0.12 | 0.27 | 1.13 | 1.75 | 1.37 | 3.14 | 7.35 | 15.3 | 12.6 | | |
| 4s | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.005 | 0.017 | 0.043 | 0.33 | 0.53 | 1.09 | 2.70 | 6.45 | 11.2 | 6.0 | 5.6 | 0.93 |
| $4p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.008 | 0.008 | 0.039 | 0.31 | 0.49 | 1.06 | 2.57 | 6.39 | 11.0 | 5.8 | 5.3 | 0.91 |
| $4p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.007 | 0.014 | 0.025 | 0.28 | 0.45 | 1.04 | 2.63 | 6.34 | 10.8 | 5.6 | | |
| $4d_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.005 | 0.010 | 0.025 | 0.17 | 0.36 | 0.96 | 2.51 | 6.09 | 10.1 | 5.0 | 4.6 | 0.92 |
| $4d_{5/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.009 | 0.024 | 0.21 | 0.29 | 0.95 | 2.50 | 6.06 | 10.1 | 4.9 | | |
| 5s | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.006 | 0.010 | 0.14 | 1.13 | 3.05 | 4.3 | 1.7 | 1.3 | 0.76 |
| $5p_{1/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.004 | 0.19 | 0.43 | 2.35 | 3.0 | 1.2 | 0.7 | 0.58 |
| $5p_{3/2}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.003 | 0.17 | 0.76 | 1.60 | 2.5 | 1.0 | 0.6 | 0.60 |

[a] Average electron shake-off energy given by Eq. (5).
[b] Relaxation energy of iodine from Ref. 23.

long as the photoelectron and shake-off electron do not come from the same principal shell. When two electrons, which are ejected due to photoionization, both come from a shell having the same principal quantum number, the experimental results are at variance with calculations based on single electron wave functions,[14] and require treatment that explicitly includes electron correlation. This has been accomplished in the case of helium.[15]

The calculations listed in Table I–IV are for a sudden creation of an inner-shell vacancy, and are not concerned with the nature of how that hole was formed. Thus, the calculations apply equally well to internal conversion or ionization by electron impact as well as photoionization. The conditions under which the sudden approximation applies have been studied in the cases of photoionization,[5b] electron impact,[16] and even proton impact.[17] For photoionization it was found that the probability for electron shake off is independent of the kinetic energy of the photoelectron when its energy is approximately three times or more than that required for the electron shake-off process. Sachenko and Burtsev[18] estimate from theory that the region where the sudden approximation is valid for photoionization is $E_{ph} \gtrsim 1.2I$–$1.3I$ where $I$ is the threshold for double ionization. Since the energy required for electron shake off is generally less than 50 eV for the outermost shell, the calculations presented in this paper will be appropriate for most x-ray photoelectron studies, where the concern is primarily with excitation in the outer shell, and where the photoelectron energies are usually in large excess of 50 eV.

From Tables I–IV one sees that the probability for electron shake off from a given subshell of a given atom increases with the number of electrons in the subshell and with the principal quantum number. The relationship between the probability for electron shake off from a shell whose principal quantum number is $n$ and the shell in which the initial vacancy is formed, $n_0$, is as follows: If $n_0 > n$, $P_{nlj}$ is negligible; if $n_0 < n$, $P_{nlj}$ increases only slightly as $n_0$ decreases until it reaches an asymptotic value; if $n_0 = n$, $P_{nlj}$ is considerably smaller than when $n_0 < n$. (However, please note our earlier comment regarding electron correlation, when $n_0 = n$; Refs. 14 and 15). These generalizations can be understood in terms of changes in the effective charge. Previously[19] a relationship was derived between electron shake off as the result of photoionization and $\beta$ decay in the same atom, viz.,

$$P_{nlj}(n_0) = P_{nlj}(\beta)\,(\Delta Z_{\text{eff}})^2, \tag{4}$$

where $P_{nlj}(n_0)$ is the probability for electron shake off as the result of a sudden removal of an electron from subshell $n_0$ of a given atom, $P_{nlj}(\beta)$ is the electron shake-off probability as the result of $\beta$ decay in the same atom and $\Delta Z_{\text{eff}}$ is the change in effective charge. In Table VI we have compared $P_{nlj}(n_0)$ for the outer shell of Xe as a function of the inner-shell vacancy, using results from Eqs. (2) and (3). For the latter we took $P_{nlj}(\beta)$ from Ref. 4 and $\Delta Z_{\text{eff}}$ from Slater's recipe[20] for screening. We see indeed that even with our crude estimate for change in effective charge the general behavior is correctly described. As one goes deeper into the core, the shake-off

TABLE V. Comparison of electron shake-off calculations (%) computed for 1s vacancy in krypton.

| $nlj$ | $P_{nlj}$ | |
|---|---|---|
| | $I$ [a] | $II$ [b] |
| 1s | 0.002 | 0.004 |
| 2s | 0.060 | 0.053 |
| 2p | 0.27 | 0.27 |
| 3s | 0.22 | 0.25 |
| 3p | 1.13 | 1.22 |
| 3d | 3.56 | 3.66 |
| 4s | 1.80 | 2.23 |
| 4p | 13.45 | 13.90 |

[a] Calculations employing relativistic Hartree-Fock-Slater wave functions.

[b] Calculations employing nonrelativistic Hartree-Fock wave functions (cf. Ref. 7).

TABLE VI. Comparison of electron-shake-off calculations (%) computed for the $5p_{3/2}$ subshell of xenon.

| Initial hole | $\lvert\Delta Z_{\text{eff}}\rvert^2$ | $P_{(\beta)}$ [a] | $P_{(n_0)}$ [b] |
|---|---|---|---|
| 1s | 1.00 | 8.51 | 8.39 |
| 2s | 1.00 | 8.51 | 7.76 |
| $2p_{1/2}$ | 1.00 | 8.51 | 7.86 |
| $2p_{3/2}$ | 1.00 | 8.51 | 7.83 |
| 3s | 1.00 | 8.51 | 7.31 |
| $3p_{1/2}$ | 1.00 | 8.51 | 7.31 |
| $3p_{3/2}$ | 1.00 | 8.51 | 7.31 |
| $3d_{3/2}$ | 1.00 | 8.51 | 7.35 |
| $3d_{5/2}$ | 1.00 | 8.51 | 7.35 |
| 4s | 0.72 | 6.13 | 6.45 |
| $4p_{1/2}$ | 0.72 | 6.13 | 6.39 |
| $4p_{3/2}$ | 0.72 | 6.13 | 6.34 |
| $4d_{3/2}$ | 0.72 | 6.13 | 6.09 |
| $4d_{5/2}$ | 0.72 | 6.13 | 6.06 |
| 5s | 0.12 | 1.02 | 3.05 |
| $5p_{3/2}$ | 0.12 | 1.02 | 2.35 |
| $5p_{5/2}$ | 0.12 | 1.02 | 1.60 |

[a] Calculation based on Eq. (4), utilizing shake-off probability for $\beta$ decay (Ref. 4) and change in effective charge ($\Delta Z_{\text{eff}}$).

[b] Calculation based on relativistic Hartree-Fock-Slater wave functions.

probability for photoionization approaches that for $\beta$ decay, which represents a unit change in effective charge. As suggested from Slater's recipe, electron removal from an outer shell does not affect the screening of an inner-shell electron, and the electron shake off should be zero, which as seen from Tables I–IV is the case.

### B. Relaxation Energy

Manne and Åberg[1] and Meldner and Perez[2] have studied the relationship between binding energy as obtained from Koopmans's theorem, viz., the eigenvalue, and the adiabatic binding energy or difference in total energy of the neutral atom and ion with a core vacancy. They derived the following expression:

$$I_R - I_0 = \sum_{i=1}^{\infty} |\langle \psi_i | \psi_R \rangle|^2 (I_i - I_0), \tag{5}$$

where $I_R$ is the energy obtained from Koopmans's theorem, $I_0$ is the ionization energy related to the normal or relaxed state. $I_i - I_0$ is the excitation energy or in our case the energy involved in electron shake up or shake off. The square of the overlap integral, $|\langle \psi_i | \psi_R \rangle|^2$, is equivalent to Eq. (1) or the probability for electron shake off. The right-hand side of Eq. (5) can be evaluated by noting that $\sum_{i=1}^{\infty} |\langle \psi_i | \psi_R \rangle|^2$ is equivalent to the total shake-off plus shake-up probabilities given by Eq. (2) and listed in Tables I–IV. The average value for $(I_i - I_0)$ can be related to the binding energy of the subshell from which shake off occurred. From a calculation of the kinetic-energy distribution of shake-off electrons by Levinger[21] it was earlier[4] estimated that

$$\langle (I_i - I_0) \rangle_{\text{avg}} = kE_B, \tag{6}$$

where $k$ is approximately 1.8.

The left-hand side of Eq. (5) is the relaxation energy and is equal to the difference between the eigenvalue and total energies as obtained[22] from relativistic wave-functions calculations by Rosén and Lindgren.[23] The relaxation energy is designated $E_R$. The evaluation of the right-hand portion of Eq. (5) is given the symbol $E_S$.

The results of calculating $E_S$ and $E_R$ are displayed in the last two columns of Tables I–IV. In general, reasonable agreement is found. The values of $E_S$ appear to be slightly lower for the inner shells and slightly higher for the outer shells. This can be best understood by critically evaluating the factor $k$ in Eq. (6). It is not surprising to discover $k$ is somewhat dependent on the nature of the atom and subshell. Comparison of the measured photoelectron spectra in neon[24] shows the experimental data had a slightly larger high-energy distribution than given in Levinger's calculations. This suggests a larger value for $k$. As one goes to the outer shells, contributions to electron shake up relative to electron shake off become more important, thus causing a decrease in $k$. It might be fair to suggest that Eq. (5) offers a way in which to obtain the average energy involved in electron shake off and shake up from a given subshell.

### C. Importance of Electron Shake off and Shake up to Photoelectron Spectra

In this section we shall discuss the importance of electron shake off and shake up to the actual photoelectron spectrum and what information the present calculations shed on this problem. First, let us consider the expression for the energy of the photoelectron which can be given as

$$E_e = h\nu - (T_f - T_i + \epsilon), \tag{7}$$

where $h\nu$ is the energy of the photon, $T_i$ and $T_f$ are the total energy of the initial atom and final ion, and $\epsilon$ is the kinetic energy of a shake-off electron. When electron shake up occurs, a discrete photoelectron peak is created, whose energy is lower than the main photoelectron peak by $(T_f^* - T_f^0)$, where $T_f^0$ and $T_f^*$ represent the total energies for the ground and excited states of the ion. When electron shake off occurs, photoelectrons appear at energies $(T_f^+ - T_f^0) + \epsilon$ below the main peak, where $T_f^+$ is the total energy for the doubly charged ion.

TABLE VII. Binding energy (eV) of outermost subshell of rare-gas ion[a] as a function of location of vacancy.

| Shell containing vacancy | Ne $(2p_{3/2})$ | Ar $(3p_{3/2})$ | Kr $(4p_{3/2})$ | Xe $(5p_{3/2})$ |
|---|---|---|---|---|
| $1s$ | 45.8 | 30.4 | 26.1 | 22.1 |
| $2s$ | 40.3 | 29.8 | 25.9 | 22.0 |
| $2p_{1/2}$ | 40.4 | 29.9 | 25.9 | 22.0 |
| $2p_{3/2}$ | 40.4 | 29.9 | 25.9 | 22.0 |
| $3s$ | | 27.5 | 25.7 | 21.9 |
| $3p_{1/2}$ | | 27.0 | 25.7 | 21.9 |
| $3p_{3/2}$ | | 27.0 | 25.7 | 21.9 |
| $3d_{3/2}$ | | | 25.7 | 21.9 |
| $3d_{5/2}$ | | | 25.7 | 21.9 |
| $4s$ | | | 24.2 | 21.8 |
| $4p_{1/2}$ | | | 23.7 | 21.8 |
| $4p_{3/2}$ | | | 23.6 | 21.8 |
| $4d_{3/2}$ | | | | 21.8 |
| $4d_{5/2}$ | | | | 21.8 |
| $5s$ | | | | 20.7 |
| $5p_{1/2}$ | | | | 20.3 |
| $5p_{3/2}$ | | | | 20.1 |

[a] Taken from eigenvalues of relativistic Hartree-Fock-Slater solutions for ions of appropriate configuration.

Since there is a continuous spectrum of energies for $\epsilon$, the photoelectron spectrum is continuous with its maximum at $\epsilon = 0$. Such continuous spectra have been observed, but when high-resolution spectroscopy is employed they are much more difficult to measure than the discrete lines from electron shake up. If electron shake off occurs from the inner shells, this would be particularly hard to observe, since the probability is lower, and the spectrum is spread out over a large energy range. The probability for electron shake up versus electron shake off is very small for inner shells, but becomes equal in magnitude as one goes to the outermost shell. Thus, since the total probability for shake off and shake up also increases as one goes to the outermost shell, the principal manifestation in photoelectron spectroscopy of excitation as the result of photoejection is the appearance of discrete lines arising from shake up of the valence-shell electrons.

The intensities of the satallite lines due to electron shake up relative to the main peak are expected to follow the observations made in Sec. III A with regard to the total probability for excitation and ionization, namely, that the intensities are nearly independent of the location of the core vacancy, increasing only slightly with decreasing principal quantum number. This prediction has been recently verified experimentally.[25]

To estimate how much the energy of the satellite lines will shift with the location of the inner-shell vacancy, we have listed in Table VII the eigenvalues for the outermost shells of the rare-gas ions as a function of the unfilled subshell. The binding energies are nearly independent of the location of the hole. Only when the vacancy is created in the outermost shell is there a significant change, and even this is only about 10%. The behavior of the ionization potentials should be reflected in the behavior of the excitation energy. Thus, the energies of the satellite peaks arising from electron shake up should be nearly unaffected by the location of the core vacancy. Some spin coupling between the vacancy in the core and the vacancy in the outermost shell will give rise to extra structure in the electron shake-up spectrum (cf. the case of photoionization of neon[13]), and this will be dependent on the location of the core hole. However, these effects may still be regarded as secondary.

Although electron shake off is not easily observed by means of the satellite continuum in a photoelectron spectrum, its effect is felt in the loss of intensity for the main peak. In addition, the relaxation energy will depend as much or more on the nature of electron shake off than on electron shake up. Thus, the extent of the satellite structure due to electron shake up will not necessarily reflect the relaxation energy associated with photoionization in a given shell.

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[10]Equation (3) is slightly altered from Eq. (3) of Ref. 4. The latter expression is suitable for electron shake off in $\beta$ decay, but is not quite appropriate for core vacancies formed in photoionization. Equation (3) of this paper is appropriate for electron shake off in both $\beta$ decay and photoionization.

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