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Addendum: Spectral Distribution of Atomic Oscillator Strengths

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The following notes outline significant advances which have come to our attention since the original paper (RMP68) went to press. They are written in the context of RMP68 and cross referenced to its Sections, page numbers, Figures, and Bibliography. The material selection has been subjective, as it was in RMP68.

(1) A rather successful effort has been made (CMcD68) to improve the calculated photoionization cross section of Li over a 5-eV range above threshold by a successive-approximation, Brueckner–Goldstone procedure. This procedure follows the general approach of Sec. 5.3 but starts from a Hartree–Fock approximation (Sec. 5.5c) which includes all intrachannel effects in zero order. The zero-order results fall ~20% below the HC67 measurements; thereby they fail to reproduce the agreement reported by a supposedly equivalent calculation (Se67). This initial approximation also yields an ~10% discrepancy between the "length" and "velocity" results corresponding to Eqs. (2.3) and (2.8); this discrepancy is analyzed in detail consistent with the discussions in Secs. 5.4 and 5.5. An interesting feature of (CMcD68) is the progressive reduction of the gaps between calculated and experimental values, as well as between the length and velocity results, in the course of successive approximations. Simultaneous improvement of the ground- and continuum-state wave functions appears essential to this end (see below).

(2) As stressed in Sec. 5.4, agreement between the "length" and "velocity" formulas [required by the consistency equation (2.6)] is present in an initial independent electron approximation but gets lost in successive approximations unless the improvements in the ground- and continuum-state wave functions fulfil conditions that remain unspecified. The violation of (2.6) which results from improving the continuum function *alone* in accordance with (6.5) and (6.6) is illustrated by the following identity (St69)‡:

$$(\psi_0 \mid v_z \mid \Psi_E) = -i\hbar^{-1}(E-E_0) \left\{ (\psi_0 \mid z \mid \psi_E) + \int d\epsilon \, \frac{\epsilon-E_0}{E-E_0} (\psi_0 \mid z \mid \psi_\epsilon) \frac{\mathcal{P}}{E-\epsilon} (\epsilon \mid K \mid E) \right\} \times [1+\pi^2 (E \mid K \mid E)^2]^{-1/2}. \quad \text{(A1)}$$

The right-hand side of (A1) should equal

$$-i\hbar^{-1}(E-E_0)(\psi_0 \mid z \mid \Psi_E)$$

in order to satisfy (2.6) but in fact differs from it by inclusion of the factor $(\epsilon-E_0)/(E-E_0)$ in the integrand. This factor introduces a departure from unity, by excess or defect, to the extent that higher approximations in the expansion (6.5) of Ψ_E include zero-order components ψ_ϵ with ϵ much larger or smaller than E.

(3) Light with $h\nu = 66.6$ eV, an emission line of nitrogen, photoionizes He, leaving the ion in either its $n=1$ or $n=2$ state and thus produces photoelectrons of either 42.0 or 1.2 eV. The observed intensity ratio of these electron groups is 0.08 ± 0.02 (Sa69). This ratio can be compared with a prediction from the profile of the $2s2p$ excitation line in Fig. 27(a). According to the discussion of Eq. (8.7), the ratio should be $\frac{1}{2}\pi q^2 \rho^2 \Gamma / \Delta E$; taking $q=2.8$, $\rho=1$, $\Gamma=0.038$ eV from (MC65), and $\Delta E = dE_s/ds = 27.2$ eV$/(1.61)^3$ in accordance with page 447, one obtains 0.07.

(4) Newer evidence has emerged on the systematic variation along the periodic system of a prominent nonhydrogenic feature of the absorption spectrum, mentioned briefly at the end of Sec. 4.8 and elsewhere in Secs. 4.6, 4.7, and 4.8. This evidence concerns the evolution and disappearance of the "resonance near threshold" of absorption by inner subshells throughout the first set of transition elements and throughout the rare earths. The new data concern the $3p(M_{\text{II,III}})$ thresholds from Ti to Ni (SHK69) and the $3d(M_{\text{IV,V}})$ threshold in Yb (CSW68); they are to be combined, respectively, with the Cu (HKSS68) data and with the extensive observations on the rare-earth $4d(N_{\text{IV,V}})$ § thresholds (ZFGZh67, FZGZh67). The rare earths with lower Z show a gradual rise of absorption near the edge with extensive broad-line structures superposed on it (FZGZh67); the gradual rise was attributed in RMP68 to the same centrifugal effect as in Xe (Sec. 4.7) and the lines to unspecified crystal-structure properties of the metal-film absorbers. The lower-Z transition elements also show a gradual rise which, however, is not matched by the corresponding absorption of Ar near its first threshold; some structure is observed, notably in Cr near the resonance maximum. These effects extend over a 5–10-eV spectral

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‡ Equation (A1) is readily generalized to a multichannel treatment as indicated on p. 484, Footnote 25.

§ The discussion of rare-earth data in RMP68 indicated this subshell erroneously at times as $4d(M_{\text{IV,V}})$ and at times as $3d(M_{\text{IV,V}})$.

range and thus are not readily fitted among the crystalline properties of such widely studied materials. [Unexplained effects have also emerged from the comparison of solid and gaseous Xe and Kr spectra (HKSK69).] The absorption rise near threshold appears to be preceded, at least in some of the transition elements as well as in rare earths (Fig. 15), by a *dip* not unlike that observed in the profiles of autoionizing lines (Fig. 27*). This observation suggests that the inner-shell absorption peak due to the "resonance near threshold" may interfere with the background absorption by outer shells much as it does (Sec. 8.1) for discrete levels broadened by autoionization. This suggestion implies the occurrence of even stronger effects of spectral repulsion than we anticipated in Sec. 8.2.

The resonance near threshold should disappear, with increasing atomic number Z, when the threshold energy overtakes the point of zero of the radial integral $R(nl,\epsilon\ l+1)$. It was noted in Secs. 4.6 and 4.7 that this occurrence tends to coincide with the Z value at which the $(n,\ l+1)$ subshell is just completed. This coincidence has now been demonstrated. The $3p$ absorption exhibits a sharp threshold jump ratio of 1.6 in Ni (whose configuration includes a $3d^8$ group) but does not even exhibit a clear threshold in the next element, Cu (Fig. 13), which has a full $3d^{10}$ group. The $3d$ absorption of Yb (presumably analogous to the $4d$ absorption for reasons noted on p. 461) shows a strong peak in trivalent compounds with a $4f^{13}$ group but not in divalent compounds with a full $4f^{14}$ complement (CSW68).† This peak is attributed in CSW68 to absorption into a discrete state $4f_{7/2}$, but the $3p$ rise in Ni clearly corresponds to the onset of a continuous absorption.

(5) Calculations based on the independent electron model of Sec. 4 and utilizing the Herman–Skillman nonhydrogenic central field (CF67, MC68) have been extended by a modified technique (McG68). The numerical potential (HS63) is represented in a succession of radial intervals by hydrogenic potentials with suitably fitted inner and outer screening (Sec. 4.3); thereby the radial wave functions become piecewise analytic. Photoionization cross sections have been obtained for each element from He to Xe and for energies from threshold to $\sim$10 times the K-shell threshold. The accuracy and cost of this procedure appear comparable to those of earlier work. No significant new feature has been detected in the newer extensive results.

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St69	A. F. Starace (unpublished), based on earlier notes by S. T. Manson.

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* The dip in Fig. 27(a) and (c) occurs on the high-, rather than low-, energy side of the peak because q happens to be negative for the examples shown.

† The observation of a $4d$ peak in the supposedly divalent Yb metal films (ZFGZh67) is now attributed to film oxidation to a trivalent state, which should occur under the experimental conditions.