oretical calculations and using experimental data on polarizabilities, refractive indices, and Verdet constants.[14] There are available also theoretical and measured values of some of the oscillator strengths occurring in (26). To calculate C, the available oscillator strengths were extended and modified in such a way that a large number of sum rules were exactly satisfied. It was ensured, in particular, that the derived oscillator strengths yielded S_{-1} accurately since the form of (26) is similar to the product of two such summations. The resulting accuracy is largely determined by the accuracy with which S_{-1} is known, S_{-1} being essentially the dipole polarizability. In none of the cases given in Table I[14] should the error exceed 20% and it is usually very much less.

TABLE I. Values of van der Waals coefficients C in atomic units.[a,b]

	H	He	Ne	Ar	H_2[c]
H	6.5	2.8	5.7	20.2	9.2
He	2.8	1.5	3.1	9.9	4.2
Ne	5.7	3.1	6.6	20.6	8.6
Ar	20.2	9.9	20.6	68.1	29.6
H_2[c]	9.2	4.2	8.6	29.6	13.3
Li	67	22	48	200	88
Na	74	25	52	210	96
K	99	33	68	280	128
Rb	100	34	69	280	132
Cs	120	38	77	320	148

[a] The interaction energy is $[-C/(r/a_0)^6][e^2/a_0]$, a_0 being the Bohr radius.

[b] Values for additional systems are given in the references. (See reference 14.)

[c] The H_2 values are averages over all orientations.

ACKNOWLEDGMENT

I am indebted to Professor J. O. Hirschfelder for encouraging me to present this account of summation techniques.

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REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

Sensitivity of $L_1L_{2,3}M_{4,5}$ Coster–Kronig Transition Rates to Variations in Energy Levels and Screening Parameters

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STUDY of the $L_1L_{2,3}M_{4,5}$ Coster–Kronig transition rates offers a sensitive tool for comparisons of various atomic wave functions. These transitions are sensitive to different screening parameters arising from use of different wave function computations and also have pointed up several inconsistencies in tabulated energy-level values. While there are many transitions of the Coster–Kronig type,[1–3] the $L_1L_{2,3}M_{4,5}$ have the features of large transition rates, sharp cutoffs at various atomic numbers, and greater proportion of the very scanty data on such transitions.

This class of transition, first described by Coster and Kronig in 1935,[1] is distinguished by the filling of a deep vacancy in an atom by another electron of the same shell, but different subshell, with ejection of another electron of different shell with low energy. The final doubly ionized state serves as the initial state for emission of x-ray satellite lines of relatively high intensity, relative to the parent lines. Because of the nature of the variations of energy levels with atomic number, these transitions are energetically possible only for certain regions of atomic number.[2–4] The general features of these transitions and their consequences have been reviewed by Burhop[3] and more recently by Listengarten.[4] The current work is concerned only with the $L_1L_{2,3}M_{4,5}$ transitions, hereafter called LLM transitions. Only a few previous calculations have been made of transition rates for the LLM transitions, including those of Ramberg and Richtmyer[5] for Au, based on the Thomas–Fermi field, of Pincherle[6] using hydrogenic functions, and of Rubinstein and Snyder[7] using a SCF function for Kr. The present calculations cover the atomic number region from Sc to Sn.

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These calculations are based on methods similar to those for the KLL transitions.[8] The transitions arise from the electrostatic interaction of two electrons in an initially deeply ionized atom, according to the theory of Wentzel.[9] The interaction is treated using screened hydrogenic functions and the Gordon continuum wave function for the ejected electron.[10] The appropriate matrix elements for the transition rates are of the form $(ab|1/r_{12}|cd)$, and are separated into radial and angular parts by the usual expansion of $1/r_{12}$ in Legendre polynomials, with the angular factors being given in Condon and Shortley.[11] For the LLM transitions considered, only P and F terms are found.

The energy of the ejected electron is quite low, below 165 eV for atomic numbers below the cutoff at Sn. The energy is taken as

$$k = [(E_1 - E_i - E_j^*)/13.605]^{\frac{1}{2}}\,, \qquad (1)$$

where k is in atomic units; E_1 is the L_1 energy-level of the atom of number Z; E_i is the L_i energy-level value; E_j^* is the M_j energy-level value for the $Z + 1$ atom. The choice of the M-level energy for the $Z + 1$ atom is taken to account for the ionization in the L_1 level. Unlike the KLL case treated by Bergstrom and Hill,[12] there is no available experimental data to indicate that a choice of $Z + c$, where c is a constant less than 1, would be preferable.

The choice of screening constants for the $3d$ electron proved to be of considerable interest and significance. These constants were taken according to the usual definition of Hartree[13] as

$$\sigma = Z - (\bar{r}_{\mathrm{H}}/\bar{r})\,, \qquad (2)$$

where σ is the screening constant; $\bar{r}_H$ is the mean hydrogenic radius $1/2(3n^2 - l(l + 1) = 10.5$ for $3d$ shell; $\bar{r}$ is the mean radius for the appropriate wave function. In this work several types of wave functions were used. The initial $\bar{r}_{3d}$ values were computed from the values given by Löwdin and Appel,[14] and fitted analytically to a formula $\bar{r} = 14.1305/(Z - 14.6588)$. Other values of $\bar{r}$ based on the wave functions of Mayers[15] for Sc, As, and Xe, and of Watson and Freeman[16] for the series Zn to Kr, were kindly supplied by Dr. C. Froese.[17] From the graph of these $\bar{r}$ values, shown on Fig. 1, it is evident that a considerable divergence in this property appears for different SCF treatments of atomic wave functions. The screening constants σ_{3d} were computed from the $\bar{r}$ values based on Eq. (2) and were used in the transition rate calculations. Screening constants used for the L_1 and $L_{2,3}$ functions were those derived in Reference 8.

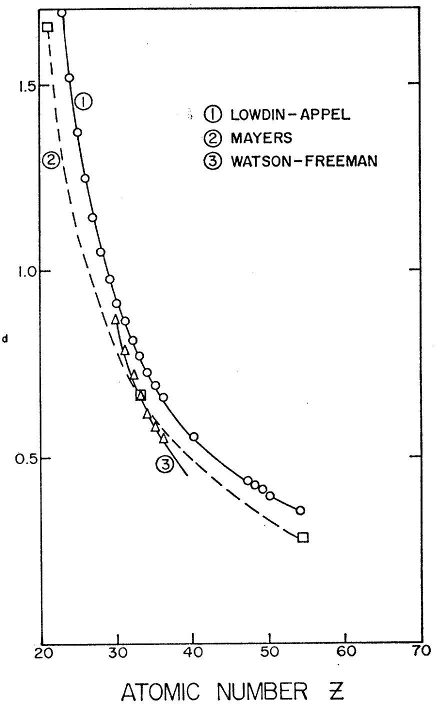

FIG. 1. Comparison of $\bar{r}_{3d}$ as a function of atomic number Z for various SCF wave functions of Löwdin and Appel (reference 14), Mayers (reference 15), and Watson and Freeman (reference 16).

Since the energies of the L_2 and L_3, and M_4 and M_5 levels are slightly different, rates for each of the four transitions $L_1L_2M_4$, $L_1L_2M_5$, $L_1L_3M_4$, and $L_1L_3M_5$ were computed separately, using the proper energies from the tables of Sandstrom[18] up to Zn, and of Wapstra, Nijgh, and Van Lieshout[19] for atoms beyond Zn. The exchange integrals were computed using the same energies as the direct integrals. The

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rates for the various terms are given simply as

$$W = [(2J+1)/\eta](D \pm 3E/5)^2(\chi/30)\,, \quad (3)$$

where η is 9 for P terms, and 14 for F terms, D and E are the appropriate direct and exchange integrals, and $+$ is taken for singlets, and $-$ for triplets, in summing the integrals. χ is a weighting factor for the number of electrons in each subshell, and equals 4:6:8:12 for each of the transitions listed above, respectively. The total transition rate is then the sum of all the individual rates.

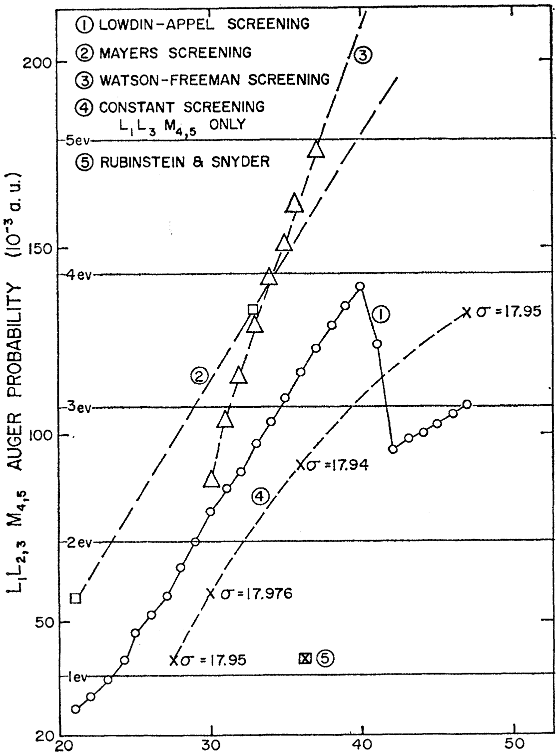

FIG. 2. Total $L_1L_{2,3}M_{4,5}$ Coster–Kronig Transition rates as a function of atomic number Z for screening constants based on $\bar{r}_{3d}$ derived from various wave functions of Löwdin and Appel (reference 14), Mayers (reference 15), and Watson and Freeman (reference 16), plus value for Kr calculated by Rubinstein and Snyder (reference 7).

The total transition rates are shown on Fig. 2 for the atoms from Sc to Ag, based on the various screening constants used. The wide variation resulting from use of different screening is apparent, both in absolute values for a given atom, and also in the slope of the transition rates for the LLM transitions as a function of atomic number. The decrease above $_{40}$ Zr is due to the disappearance of the $L_1L_2M_{4,5}$ transitions beyond this point. In this region of atomic number, the major portion of the L_1 level width is due to LLM transitions. The radiative partial width is quite small as evidenced by the low values, about 0.05, for the L fluorescence widths.[4] Also the LLN transitions are of relatively small value in this region, based on comparisons of hydrogenic probabilities at comparable k values. The total Auger widths are of the order of 3–5 eV, which leads to values of only a few tenths of an electron volt for the radiative widths. There are considerably greater variations in widths determined for differing screening constants. For comparison, Table I shows the calculated LLM transition rates for Kr and Au. It is seen that the Rubinstein and Snyder rates for Kr are considerably smaller than are found in the current calculations, and also that their P:F ratio of 1:4 is much less than the present ratios, or those of Ramberg and Richtmyer or Pincherle for Au. The values of Pincherle are considerably less than those of Ramberg and Richtmyer or the current values. The current values for Au give an LLM width of 3.67 eV based on the Löwdin–Appel screening, or 4.87 eV based on Slater screening.[20] Taking the Ramberg and Richtmyer ratio of 1.385 for the total L_1

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TABLE I. Comparison of $L_1L_{2,3}M_{4,5}$ auger transition rates.

	36 Kr					79 Au[d]			
		This work						This work	
Terms	R–S[f]	L–A[g]	M[h]	W–F[i]	S[j]	R–R[k]	P[l]	L–A[g]	S[j]
$^1P + {}^3P$	10.64	1.43		1.00	1.53	30.39	2.26	0.57	3.05
$^1F + {}^3F$	39.00	115.84		161.65	97.31	285.55	63.68	130.66	171.16
Total[a]	49.64	117.27	157[c]	162.64	98.85	315.94	65.94	131.23	174.21
Total, eV[b]	1.35	3.28	4.3	4.43	2.70	8.60	1.79[e]	3.67	4.87

[a] Values given in 10^{-3} a.u.
[b] 1 a.u. = 27.21 eV; 1 eV = 36.75 × 10^{-3} a.u.
[c] Projected value.
[d] Only $L_1L_3M_{4,5}$ Transitions energetically possible.
[e] Total L_1 width given as 5.5 eV in reference 5.
[f] R–S Rubinstein and Snyder (reference 7).
[g] L–A Löwdin–Appel basis (reference 14).
[h] M Mayers basis (reference 15).
[i] W–F Watson–Freeman basis (reference 16).
[j] S Slater basis (reference 20).
[k] R–R Ramberg and Richtmyer (reference 5).
[l] P Pincherle (reference 6).

Auger width to the LLM width, and using their value of 1.78 eV for the radiative width, the total L_1 width would be found as 6.9 eV and 8.5 eV for the Löwdin–Appel and Slater screening, respectively, compared to the Richtmyer observed width of 8.7 eV for the L_1 level of Au. The agreement is satisfactory. In the case of Kr, there is no direct measurement of L_1 level width as yet reported.

What is most interesting in these results is the possibility of experimental determination of the most appropriate calculated wave functions. Determinations of L_1 level widths for several atoms such as Zn, Kr, and Zr would allow both the total magnitudes and their slopes with atomic number to be compared with the calculated values. Either through absorption-edge measurements of considerable difficulty, or through photoelectron methods, such as those of Siegbahn and his co-workers,[21] one can expect sufficient accuracy to permit discrimination of the preferred screening, and, hence, of the more appropriate wave function. In the case of Kr the values derived on the basis of the Watson and Freeman $\bar{r}$ correspond to an LLM width of about 4.7 eV, compared to the value of about 3.3 eV based on the Löwdin and Appel $\bar{r}$, or about 4.3 eV based on a linear projection of values based on Mayers $\bar{r}$. It is also worthy of note that the LLM transition rates are quite linear with atomic number in this region, and reasonable projections can be made. The slope of the Watson–Freeman based rates is also much greater than that of the Löwdin–Appel based rates. Although the Mayers data cover only three elements, the concordance of slope of $\bar{r}$ with that of Löwdin–Appel would show a similar concordance of slope in the transition rates, or in effect, merely a shift upwards in the curve of LLM transition rate vs atomic number. Projecting these curves to Zr, the LLM widths would become about 5.3 eV, 5.0 eV, and 3.9 eV for the Watson–Freeman, Mayers, and Löwdin–Appel bases, respectively. Taking the total L_1 level width as 1.2 times the LLM width to account for radiative width and LLN and other transitions, which is reasonable in this region of atomic number, the respective L_1 level widths would become 6.4 eV, 6.0 eV, and 4.7 eV. In conjunction with the varied slopes, x-ray measurements could distinguish among these values. The differences between different wave functions are of much greater magnitude for these LLM transitions than are evidenced on the basis of energy criteria for the wave functions.

Also in the course of the calculations, the sensitivity of the LLM transition rates to energy of the ejected electrons was demonstrated. These rates do not show any maxima in the range of atomic numbers considered, except where energy cutoffs prohibit a particular $L_1L_iM_j$ transition. The matrix elements show a continuous increase with atomic number, even though the ejected electron energy goes through a maximum, dropping to less than 10 eV near the cutoff atomic number, in contradistinction to previous surmise.[1–3] The total rates are rather linear as has been mentioned, and some discrepancies in energy level tables were noted as a result of this.

In the case of the LLM transitions in Zn and Ga, using the energy-level data from Sandstrom's tables,[19] a large deviation from the general trend of values for the matrix elements was noted. This was traced to a K-level energy value for Ga of 10395 eV, which affected the L_2,L_3- and $M_{4,5}$-level values, and thus both the Zn and Ga LLM transition rates. The same K-level value in the tables of Wapstra *et al.*[20] was 10369 eV, which resulted in the LLM rates falling closely on the trend line. In the case of Kr, Wapstra's table gave a value of 1904 eV for the L_1 level, which also resulted in a discrepancy. A value of about 1920 eV fitted the trend closely, and was taken as appropriate. It was later found that Moore[22] had redetermined the Kr energy levels, finding a value for the L_1 level of 1920 eV. No other major discrepancies, other than obvious misprints, were noted in the tables. Some possible minor discrepancies have been suspected, but cannot be unambiguously specified. Typical is the case of As, where the LLM transition rates seem slightly low, but no tabulated level value departs from expected values by more than a few eV. Sandstrom's K level for Ge is 4 eV lower than Wapstra's, and for As is 3 eV higher. Since the M-level energy is based on the K level, taken for $Z+1$, this over-all difference of 7 eV could lead to an explanation of the low transition rate. Closer study with more exact wave functions is indicated.

The results of the calculations described show the value of the $L_1L_{2,3}M_{4,5}$ Coster–Kronig transitions as a vehicle for both experimental and further theoretical study on various facets of atomic structure. In the present work, no attempt has been made to include any effects of intermediate coupling, nor have any relativistic effects been considered. These effects should be minor, in the region covered, since only total rates are concerned here, rather than term intensities.

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The author would like to express his deep appreciation to P. Nikolai and W. L. McDavid of these laboratories for invaluable assistance in numerical analysis and programming phases of this work, and would also like to acknowledge that the computations were performed on the IBM 7090 computer of the Aeronautical Systems Division, Wright–Patterson Air Force Base, Ohio.

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Spin Resonance and Hyperfine Interaction

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INTRODUCTION

THIS paper is restricted to electron spin resonance phenomena in free radicals. We shall choose a few topics in which significant advances have been made recently, especially topics reflecting more directly on some aspects of electron correlation. We shall, therefore, largely be concerned with discussing the electron spin resonance (ESR) spectra of organic free radicals. These species exhibit electron spin resonance because they have an unpaired π electron.

The spin Hamiltonian $\mathcal{H}$ for a system of π electrons such as one has in a π-electron radical can be written as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \,, \tag{1}$$

where

$$\mathcal{H}_1 = \mathcal{H}_0 + \beta \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} \tag{2}$$

and

$$\mathcal{H}_2 = g_e\beta_e g_N\beta_N \sum_{\lambda,\mu}\left[-\frac{\mathbf{S}_\lambda\cdot\mathbf{I}_\lambda}{r^3_{\lambda\mu}} + 3\,\frac{(\mathbf{r}_{\lambda\mu}\cdot\mathbf{S}_\lambda)(\mathbf{r}_{\lambda\mu}\cdot\mathbf{I}_\mu)}{r^5_{\lambda\mu}}\right] + \frac{8\pi}{3}\,g_e\beta_e g_N\beta_N \sum_{\lambda\mu}(\mathbf{S}_\lambda\cdot\mathbf{I}_\mu)\,\delta(\mathbf{r}_{\lambda\mu}) \,. \tag{3}$$

For radicals in solution (or in the gas phase) the term between [ ] in Eq. (3) averages out to zero,[1] so for these cases the second term, the Fermi contact interaction which is isotropic, is important and gives rise to the hyperfine splitting observed for free radicals in solution. Weissman[1] neglected spin-orbital interaction effects which can also lead to isotropic hyperfine splittings for radicals in solutions[2]; but the effects are about 100 times too small to account for any of the observed splittings in aromatic free radicals. Considering, therefore, only the hyperfine interaction between the z components of the electron and nuclear spins (valid in the Paschen–Back region), the Fermi contact Hamiltonian which gives the nonvanishing isotropic hyperfine splitting for free radicals in solution is

$$\mathcal{H}_N = \frac{8\pi g|\beta|}{3}\left(\frac{\mu_N}{I}\right)\sum_k S_{kz}I_{Nz}\delta(\mathbf{r}_{kN}) \,. \tag{4}$$

In Eq. (4) $|\beta|$ is the absolute magnitude of the Bohr magneton, $\delta(\mathbf{r}_{kN})$ is the Dirac delta function of the distance $\mathbf{r}_{kN}$ between electron k and nucleus N, μ_N is the magnetic moment of proton N, and I_{Nz} is the z component of the spin of proton N, in units of $\hbar$. This equation can be expressed more simply in terms of the "coupling constant" for the proton N, a_N as

$$\mathcal{H}_N = h a_N S_z I_{Nz} \,. \tag{5}$$

SPIN DENSITIES IN π-ELECTRON RADICALS

Equation (5) is frequently written in the form introduced by McConnell[3]

$$a_N = Q\rho_N \,. \tag{6}$$

Here Q is negative and has been given various values such as -22.5 G for the benzene negative ion,[4] -25.67 G for the cyclooctatetraene radical anion,[5] and values of about -30 G,[6] which are necessary to fit the observed electron spin resonance spectra of polynuclear hydrocarbon radical ions, if it is assumed that the odd electron densities ρ_N's are given by the

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