Relativistic effects on transition probabilities in the Li and Be isoelectronic sequences*

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We have evaluated relativistic dipole oscillator line and momentum strengths for a number of elements in the Li and Be isoelectronic sequences. In the Li sequence, the transitions considered are $2s_{1/2}$-$2p_{1/2,3/2}$, $2s_{1/2}$-$3p_{1/2,3/2}$, $2p_{1/2}$-$3d_{3/2}$, and $2p_{3/2}$-$3d_{3/2,5/2}$; in the Be sequence, $2s^2_{1/2}$-$2s_{1/2}2p_{1/2,3/2}$. The two electromagnetic-field gauges which in the nonrelativistic limit give the length and velocity forms of the transition operator have been used. The heaviest element considered in both sequences was uranium. Relativistic wave functions were obtained using a multiconfiguration Dirac-Hartree-Fock calculation. Nonrelativistic calculations of similar accuracy were also carried out for comparative purposes. The results are discussed with a particular emphasis on how relativistic effects manifest themselves, and under what conditions.

I. INTRODUCTION

The study of transition probabilities in highly ionized atoms is a subject of considerable interest for many fields. For example, transition probabilities are very important in studies of controlled thermonuclear reactions, where atomic radiation is one of the primary loss mechanisms. They are also important in astrophysical studies, where accurate transition probabilities are necessary in the determination of atomic abundances. Beam-foil spectroscopy has, of course, recently provided a new method of accurate measurement of transition probabilities in highly ionized atoms, thus providing both a test of previous predictions and a direct challenge to theoreticians to explain newly measured values.

Since in a highly ionized atom the electrons move in the field of a large effective nuclear charge, one expects to see relativistic effects in such quantities as transition energies and probabilities. The basic techniques necessary for the evaluation of these effects are, of course, almost as old as quantum mechanics itself, being based on the Dirac equation.[1] However, these techniques tend to be rather complicated mathematically or computationally, in particular if they involve self-consistent-field calculations.[2,3]

Early self-consistent-field studies of relativistic effects[3] were confined primarily to neutral or only-a-few-times-ionized atoms, since these were of primary experimental interest. However, with the conjunction of the interest in highly ionized atoms, mentioned above, and the availability of high-speed computing equipment, efforts[4] are now being made to carry out accurate self-consistent studies of large numbers of ions.

Our primary emphasis will not be on the prediction of a specific number, for example, the oscillator strength of a particular line, but rather on an overall study of the regions in which relativistic effects may be important, and a determination of just how these effects manifest themselves. This paper marks the first of a series of papers in which we will seek to obtain at least partial answers to these questions of where and how.

The relativistic Dirac-Hartree-Fock[3] (DHF) method would seem to be, at least in principle, the method most likely to produce accurate relativistic wave functions in highly ionized atoms. In addition, by using multiconfiguration DHF calculations, one can take into account in a straightforward manner some of the most important correlation effects. We do not claim, however, to have included all correlation effects in our calculations, since we are interested primarily in understanding relativistic effects, and not in calculating the very accurate numbers which only very sophisticated correlation calculations can produce. Thus, for example, our study of the Be sequence involves only the two ground configurations $2s^2$ and $2p^2$ and the single-excited configuration $2s2p$; the correlation calculation of Burke, Hibbert, and Robb[5] utilized a total of 13 configurations. We show below, however, that the effects of correlations not included in our work seem to decrease rapidly with increasing Z.

Grant[6] has recently discussed the importance of gauge transformations for relativistic transition probabilities calculated using approximate wave functions such as those obtained from a DHF calculation. He also obtained the two gauges which for the electric dipole case reduce in the nonrelativistic limit to the usual length and velocity forms of the transition probability. Since we wish to compare our relativistic results to those obtained from nonrelativistic calculations in order to see the effects of relativity, we have carried out calculations in both of these gauges. Results of these calculations for the Li and Be isoelectronic sequences are described in Sec. III.

In Sec. II we discuss the theory of relativistic transition probabilities. We repeat Grant's[6] analy-

sis in Sec. II A and II B, since our results differ from his by an overall multiplicative factor and by phase factors which cannot be explained by differences in coupling. An alternative method of analyzing relativistic effects—effective operators[7]—is described in Sec. II C. The specific relationships of the relativistic oscillator, line, and momentum strengths to the transition operators of Sec. II A are discussed in Sec. II D. Finally, in Sec. IV we discuss our results with an emphasis on beginning to answer the question of how and where outlined above.

II. THEORY

A. Relativistic transition operators

The interaction Hamiltonian responsible for the electromagnetic transitions in an N-electron atom is, in covariant form,[8]

$$H_{\rm int} = \sum_{j=1}^{N} ie\gamma_4(j)\gamma_\mu(j)A^\mu(x_j)\,, \tag{1}$$

where the sum is over the N electrons in the atom. $A^\mu(x)$ is the quantized photon field $[A=(\vec{A},i\varphi)]$

$$A^\mu(x) = \sum_\gamma [a_\gamma A^\mu_\gamma(x) + a^\dagger_\gamma (A^\mu_\gamma(x))^*] \tag{2}$$

(we will use Gaussian units in this work). Here, $a^\dagger_\gamma$ and a_γ are creation and annihilation operators, respectively, for photons of type γ; $A^\mu_\gamma(x)$ is the field amplitude at x $[x=(\vec{r},ict)]$; and the electron charge is $-e$. The γ_μ matrices are defined by

$$\vec{\gamma} = -i\beta\vec{\alpha}\,, \quad \gamma_4 = \beta, \tag{3}$$

where $\vec{\alpha}$ is expressed in terms of the Pauli spin matrices $\vec{\sigma}$:

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}. \tag{4}$$

The metric tensor $g_{\mu\nu}$ is simply I, the 4×4 identity matrix. For the case in which A^μ is expanded in terms of photons of definite angular momentum L, projection M and energy $\hbar\omega$, Eq. (2) becomes

$$A^\mu(x) = \sum_{\omega LM}\sum_{\lambda=0}^{1} [a^{(\lambda)}_{\omega LM} A^\mu_{\omega LM\lambda}(x) + a^{\dagger(\lambda)}_{\omega LM}(A^\mu_{\omega LM\lambda}(x))^*]\,, \tag{5}$$

where $\lambda=1$ stands for a photon of electric type, and $\lambda=0$ a photon of magnetic type.

Electric-type field amplitudes which satisfy the Lorentz condition are given by[8]

$$\vec{A}_{\omega LM1}(x) = i^{L+1}\left(\frac{4\pi\hbar\omega}{R}\right)^{1/2}\left\{\left[\left(\frac{L}{2L+1}\right)^{1/2} j_{L+1}\vec{Y}_{L,L+1,M} - \left(\frac{L+1}{2L+1}\right)^{1/2} j_{L-1}\vec{Y}_{L,L-1,M}\right] - G\left[\left(\frac{L+1}{2L+1}\right)^{1/2} j_{L+1}\vec{Y}_{L,L+1,M} + \left(\frac{L}{2L+1}\right)^{1/2} j_{L-1}\vec{Y}_{L,L-1,M}\right]\right\} e^{-i\omega t} \tag{6}$$

and

$$A^4_{\omega LM1}(x) = i^{L+1}(4\pi\hbar\omega/R)^{1/2} G j_L Y_{LM} e^{-i\omega t} \equiv i\varphi_{\omega LM1}\,. \tag{7}$$

The quantities $j_L \equiv j_L(\omega r/c)$ are spherical Bessel functions, and the $\vec{Y}_{L,J,M}$ are vector spherical harmonics as defined by Akhiezer and Berestetskii.[8] The quantity R is the radius of a large sphere in which the waves are confined. The constant G reflects the possibility of a restricted gauge transformation within the Lorentz gauge, i.e., for potentials satisfying the Lorentz condition

$$\partial A^\mu/\partial x_\mu = 0\,,$$

one can make the gauge transformation

$$\vec{A} \to \vec{A} + \vec{\nabla}\Lambda\,, \quad \varphi \to \varphi - \frac{1}{c}\frac{\partial\Lambda}{\partial t}\,, \tag{8}$$

where $\Box^2\Lambda = 0$. The part of $A_{\omega LM1}$ containing G describes a longitudinal photon; the remainder describes a transverse photon. It is the transverse nature of the observable $\vec{E}$ and $\vec{B}$ fields which forces the arbitrary constant G to be the same for the longitudinal vector field and the scalar field. The corresponding magnetic field amplitudes are given by[8]

$$\vec{A}_{\omega LM0} = i^L(4\pi\hbar\omega/R)^{1/2}\vec{Y}_{L,L,M} j_L e^{-i\omega t}\,, \quad A^4_{\omega LM0} = 0\,. \tag{9}$$

The transition amplitude is given, in first-order perturbation theory, by

$$\mathfrak{M}(t) = (J_f M_f; n_f | H_{\rm int} | J_i M_i; n_i)\,, \tag{10}$$

where J_f and M_f are the total angular momentum and z projection of the angular momentum for the final atomic state and J_i and M_i are the corresponding quantum numbers for the initial atomic state. The numbers n_f and n_i are the numbers of photons present in the final and initial states, respectively. Using Eqs. (1) and (5), we see that if

$n_i = n_f + 1$ (absorption), only the term containing A^μ will contribute to $\mathfrak{M}$; if $n_f = n_i + 1$ (emission), only the term containing $(A^\mu)^*$ will contribute. We denote the resulting expressions for $\mathfrak{M}$ by $\mathfrak{M}_a$ and $\mathfrak{M}_e$, respectively.

The differential transition rate dW can be directly related to $\mathfrak{M}$ using standard first-order perturbation theory. For example, if the initial atomic state is excited with respect to the final state, i.e., an emission, one obtains

$$dW = (2\pi/\hbar)\delta(E_f - E_i + \hbar\omega)\,|\mathfrak{M}_e|^2 \rho_f\,, \tag{11}$$

where ρ_f is the differential density of final photon states; $\rho_f = R\,d\omega/\pi c$ for the normalization used in Eqs. (6)–(8). The δ function is a statement of conservation of energy. Integrating over energy, one obtains the total probability of emission of a photon in going from the atomic state $|J_i M_i)$ to the atomic state $|J_f M_f)$:

$$W_e = (2R/\hbar^2 c)\,|\mathfrak{M}_e|^2\,. \tag{12}$$

When A^μ is given by Eq. (5), one can put Eq. (10) into a form which is more useful for calculations by using the tensorial nature of the operators. Thus, either $\mathfrak{M}_e$ or $\mathfrak{M}_a$ can be written in general form

$$\mathfrak{M} = (-1)^{J_f - M_f}(n)^{1/2} \sum_{\omega L M \lambda} \begin{pmatrix} J_f & L & J_i \\ -M_f & M & M_i \end{pmatrix} \times (J_f \| \sum_j h_{\omega L \lambda}(j) \| J_i)\,, \tag{13}$$

where n is the number of photons present after emission ($\mathfrak{M}_e$) or before absorption ($\mathfrak{M}_a$), and the operator $h_{\omega L\lambda}$ is defined by

$$h_{\omega L\lambda} = \begin{cases} ie\gamma_4\gamma_\mu A^\mu_\gamma\,, & \text{for } \mathfrak{M}_a\,, \\ ie\gamma_4\gamma_\mu (A^\mu_\gamma)^*\,, & \text{for } \mathfrak{M}_e\,. \end{cases} \tag{14}$$

The symbol $(\cdots\|\cdots\|\cdots)$ represents a reduced matrix element.[9] Using the usual rules[9] for evaluating many-particle reduced matrix elements, one obtains, finally,

$$\mathfrak{M} = (-1)^{2J_f - M_L - L}(n)^{1/2} \sum_{\omega L M \lambda} \begin{pmatrix} J_f & L & J_i \\ -M_f & M & M_i \end{pmatrix} [J_f, J_i]^{1/2} \times \sum_{J_c, j_f, j_i} (-1)^{J_c + j_i} \begin{pmatrix} J_f & L & J_i \\ j_i & J_c & j_f \end{pmatrix} (J_f \| J_c, j_f)(J_i \| J_c, j_i)(j_f \| h_{\omega L\lambda} \| j_i)\,. \tag{15}$$

The quantities $(\cdots\|\cdots)$ are coefficients of fractional parentage (CFP's) for the entire N-electron system (not just the open shell). Such CFP's have been discussed in the LS-coupling case by one of us[10]; extension to jj coupling is straightforward. The symbol $[a, b, \cdots] = (2a+1)(2b+1)\cdots$.

We now consider evaluation of the one-electron reduced matrix element which appears in Eq. (15). In order to do so unambiguously, we must specify the coupling convention which we use in defining our relativistic single-electron states. Our one-electron states are of the type

$$|n\tfrac{1}{2}ljm) = \begin{pmatrix} (1/r)F_{nlj}\,|\tfrac{1}{2}ljm\rangle \\ (i/r)G_{nlj}\,|\tfrac{1}{2}\bar{l}jm\rangle \end{pmatrix}, \tag{16}$$

where

$$|\tfrac{1}{2}ljm\rangle = \sum_{m_s, m_l} (-1)^{l-1/2-m} \begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m_l & -m \end{pmatrix} \times [j]^{1/2} \chi_{m_s} Y_{lm_l}\,.$$

χ_{m_s} is a two-component spinor, and $\bar{l} + l = 2j$.

First, consider electric-type interactions. Using the relationship[7]

$$\vec{\alpha}\cdot\vec{Y}_{LKM} = (-1)^{L+K+1}[(2K+1)/4\pi]^{1/2}(\alpha C^{(K)})^L_M\,, \tag{17}$$

where $C^{(k)}_q = [4\pi/(2k+1)]^{1/2} Y_{kq}$, and expressions for reduced matrix elements[7] of the operators $C^{(k)}$ and $(\alpha C^{(k)})^{(L)}$, one obtains

$$(j_f \| h_{\omega L1} \| j_i) = [G(\mathcal{F}_S + \mathcal{F}_L) + \mathcal{F}_T]a\,, \tag{18}$$

where $a = i^L$ for absorption, $a = (-1)^{L+1} i^L$ for emission, and

$$\begin{aligned} \mathcal{F}_S &= [L]^{1/2} b\, J_L\,(E_f - E_i)/|E_f - E_i|\,, \\ \mathcal{F}_L &= -b[L]^{-1/2}[(\kappa_f - \kappa_i)(I^+_{L+1} + I^+_{L-1}) \\ &\qquad + (L+1)I^-_{L+1} - LI^-_{L-1}]\,, \\ \mathcal{F}_T &= b[L]^{-1/2}\left[\left(\frac{L}{2L+1}\right)^{1/2}[(\kappa_f - \kappa_i)I^+_{L+1} + (L+1)I^-_{L+1}] \right. \\ &\qquad \left. - \left(\frac{L+1}{L}\right)^{1/2}[(\kappa_f - \kappa_i)I^+_{L-1} - LI^-_{L-1}]\right]. \end{aligned} \tag{19}$$

In Eqs. (19),

$$b = e\left(\frac{\hbar\omega}{R}\right)^{1/2}(-1)^{j_f-1/2}[j_i,j_f]^{1/2}\begin{pmatrix} j_f & L & j_i \\ -\frac{1}{2} & 0 & \frac{1}{2}\end{pmatrix}, \tag{20}$$

and J_L and $I_L^{\pm}$ are radial integrals defined by[6,11]

$$J_L = \int (F_f F_i + G_f G_i) j_L \, dr\,,$$
$$I_L^{\pm} = \int (F_f G_i \pm G_f F_i) j_L \, dr\,. \tag{21}$$

$\mathfrak{F}_S$ arises from the scalar potential, $\mathfrak{F}_L$ from the longitudinal vector potential, and $\mathfrak{F}_T$ from the transverse vector potential. These equations are valid for either $\mathfrak{M}_a$ or $\mathfrak{M}_e$.

We noted above that our results differed somewhat from those of Grant.[6] Comparison of our Eqs. (18)–(20) with his Eq. (4.10) shows a sign difference in the contribution due to the scalar potential; in addition, his result is $(2L+1)^{1/2}$ larger than ours. The sign difference may arise from Grant's[6] Eq. (3.11), where there is an error in the relative signs of the scalar and vector terms,[3] or it may be due to his[6] reduced matrix element of C^L [Eq. (4.4) of Ref. 6], which is the negative of ours.[7] The factor of $(2L+1)^{1/2}$ arises from the normalization of the second quantized field A^μ; we have used the normalization in a spherical box of Akhiezer and Berestetskii. Grant has used a δ-function normalization.

For magnetic-type interactions, one obtains immediately

$$(j_f\|h_{\omega L0}\|j_i) = -iba(\kappa_f+\kappa_i)[(2L+1)/L(L+1)]^{1/2} I_L^+\,. \tag{22}$$

B. Gauge transformations

It can easily be shown[6,8] that if both the initial and final states are exact solutions to the same Dirac equation,

$$\mathfrak{F}_S + \mathfrak{F}_L = 0\,. \tag{23}$$

That is, the gauge transformation—the specific values of G—does not have any effect on the transition rate. However, if the final and initial states are only approximate solutions to a common Dirac equation, or if they satisfy slightly different equations, then Eq. (23) will no longer be true, and the value of $\mathfrak{M}_a$ or $\mathfrak{M}_e$ will be a function of G.[6] This will be the case when the initial and final states are solutions to a DHF equation.

Grant[6] discussed the implications of this dependence of the rate on G by considering the nonrelativistic limits of $\mathfrak{M}$ for electric dipole transitions. He showed that there are two values of G which are of particular utility in that they lead to well-known nonrelativistic operators. First, if $G=0$, one has the usual Coulomb gauge result, which has as nonrelativistic limit the momentum form of the transition operator. Second, if $G=-[(L+1)/L]^{1/2}$, one obtains an expression which reduces to the usual length form of the transition operator. Since it is well known that these two operators usually give different results when Hartree-Fock wave functions are used, it is not surprising that their relativistic equivalents should give different results.

Since our goal is to study effects of relativity on transition probabilities, we must compare relativistic calculations to nonrelativistic calculations. In order to make this comparison, we have calculated transition rates using both the "length" gauge for $\mathfrak{M}$, using

$$(j_f\|h_{\omega L1}\|j_i)_L = \left(\frac{2L+1}{L(L+1)}\right)^{1/2}\beta a \times\left(-J_L\frac{E_f-E_i}{|E_f-E_i|}(L+1) + (\kappa_f-\kappa_i)I_{L+1}^+ + (L+1)I_{L+1}^-\right), \tag{24}$$

and the "velocity" gauge,

$$(j_f\|h_{\omega L1}\|j_i)_V = a\beta(2L+1)^{-1/2}\left[\left(\frac{L}{L+1}\right)^{1/2}[(\kappa_f-\kappa_i)I_{L+1}^+ + (L+1)I_{L+1}^-] - \left(\frac{L+1}{L}\right)^{1/2}[(\kappa_f-\kappa_i)I_{L-1}^+ - LI_{L-1}^-]\right]. \tag{25}$$

A third choice of gauge, $G=[L/(L+1)]^{1/2}$, leads to the dipole formulation of Babushkin.[12] However, as is obvious from the work of Grant,[6] this gauge reduces in the nonrelativistic limit to a linear combination of length and velocity forms of the dipole operator, and thus is not well suited for comparison with traditional nonrelativistic calculations.

C. Effective operators

The technique of effective operators enables one to expand relativistic operators in terms of operators having transformation properties identical to those of familiar nonrelativistic operators.[7,13,14] By studying both the relativistic effective operator and the nonrelativistic operator which is its limit

as $(v/c)^2 \to 0$, one can see directly how familiar nonrelativistic operators are changed by relativity. Effective operators are also quite useful in the interpretation of experimental data. They have, thus far, found their greatest use in studies of hyperfine structure.[13,15] We use them here to study relativistic effects on transition operators.

If $|\psi)$ is a relativistic state which has as nonrelativistic limit $|\psi\rangle$, etc., then for any relativistic operator R one can define an effective operator R_e by

$$(\psi|R|\psi') = \langle\psi|R_e|\psi'\rangle . \tag{26}$$

As shown by Armstrong and Feneuille,[7] any one-electron relativistic operator R^K which transforms as a tensor of rank K in J space can be expanded in the effective form

$$R_e^K = \sum A_{\kappa k}^K(l_1, l_2) W^{(\kappa k)K}(l_1, l_2) , \tag{27}$$

where $W^{(\kappa k)K}(l_1, l_2)$ is a double tensor operator of rank κ in spin space, k in orbital space, and K in the combined space $\vec{J} = \vec{L} + \vec{S}$. The magnitude of $W^{(\kappa k)}$ is fixed by its reduced matrix element taken between nonrelativistic states[16]:

$$W^{(\kappa k)}(l_1, l_2) = \sum_i w_i^{(\kappa k)}(l_1, l_2) ,$$
$$\langle \tfrac{1}{2} l_\alpha || \, w^{(\kappa k)}(l_1, l_2) || \tfrac{1}{2} l_\beta \rangle = [\kappa, k]^{1/2} \delta(l_\alpha, l_1) \delta(l_2, l_\beta) . \tag{28}$$

The expansion coefficient $A_{\kappa k}^K$ of Eq. (27) is given by[7]

$$A_{\kappa k}^K(l_1, l_2) = \sum_{j_1, j_2} [j_1, j_2, \kappa, k]^{1/2} [K]^{-1/2} \times \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ l_1 & l_2 & k \\ j_1 & j_2 & K \end{Bmatrix} \times (\tfrac{1}{2} l_1 j_1 || R^K || \tfrac{1}{2} l_2 j_2) . \tag{29}$$

In other words, by this technique one expresses a relativistic operator R^K in terms of constants $A_{\kappa k}^K$, which are evaluated by doing sums over relativistic matrix elements, and of operators $W^{(\kappa k)K}$, which are to be evaluated between nonrelativistic states. Since the operator P^K which R^K approaches in the nonrelativistic limit can in a natural way be expressed in terms of the $W^{(\kappa k)K}$, one is able in this way to make a very clear comparison between R^K and P^K.

In Sec. II B we evaluated the reduced matrix elements of relativistic transition operators. Thus we can immediately evaluate $A_{\kappa k}^K$ for any desired multipole. We are interested here only in the electric dipole operator, which has an expansion of the type

$$R_e^1 = \sum_{l_1, l_2} [A_{01}^1(l_1, l_2) W^{(01)1}(l_1, l_2) + A_{11}^1(l_1, l_2) W^{(11)1}(l_1, l_2) + A_{12}^1(l_1, l_2) W^{(12)1}(l_1, l_2)] , \tag{30}$$

where the A's can be obtained from Eq. (29). In terms of these operators, the matrix element $\mathfrak{M}$ of Eq. (15) can be written

$$\mathfrak{M} = \langle J_f \, M_f | R_e^1 | \, J_i \, M_i \rangle , \tag{31}$$

where $| \, J_i M_i \rangle$ is the nonrelativistic limit of state $|J_i M_i)$, etc.

In the nonrelativistic limit, $A_{12}^1 = A_{11}^1 = 0$ in both the length and velocity gauges, and

$$A_{01}^1 = -\frac{2ei}{3} \left(\frac{\hbar\omega}{R} \right)^{1/2} \frac{\omega}{c} (l_1 || C^{(1)} || \, l_2) \times \int R_{l_1} r R_{l_2} \, dr ,$$
$$A_{01}^1 = \frac{2ei}{3} \left(\frac{\hbar\omega}{R} \right)^{1/2} \frac{\hbar}{mc} (l_1 || C^{(1)} || \, l_2) \times \int R_{l_1} \left(\frac{d}{dr} - \frac{l_1(l_1+1) - l_2(l_2+1)}{2r} \right) R_{l_2} \, dr , \tag{32}$$

for the length and velocity gauges, respectively. Deviations of the A's from these values are direct indications that the optical electron is showing relativistic effects. Finally, Eq. (30) shows very clearly the way in which the usual nonrelativistic dipole operator $r \sim W^{(01)1}$ is changed by relativity, and indicates how the familiar nonrelativistic dipole selection rules on L and S must be altered by these relativistic effects.

D. Dipole oscillator, line, and momentum strengths

The most convenient way to describe the results of our calculations is not through the transition probability W of Eq. (12), but rather through closely related quantities such as dipole oscillator and line strengths. The relativistic dipole oscillator strength f is defined by (for absorption)

$$f = \frac{1}{[J_i]} \frac{mc^3}{2e^2\omega^2} \sum_{M_f, M_i, M} W_{M_f, M_i}^1 = \frac{1}{[J_i]} \frac{mc^2 R}{\hbar^2 e^2 \omega^2} \left| (J_f || \sum_j h_{\omega 1 \lambda}(j) || \, J_i) \right|^2 , \tag{33}$$

where W_{M_f, M_i}^1 is the transition probability of Eq. (12), keeping, however, only the dipole term; M is the z projection of the photon angular momentum. The quantity W^1 is calculated using Eqs. (12), (15), and either Eq. (24) or (25), for the

length or velocity forms, respectively. Grant's[6] expression for f does not include the sum over M, which has the effect of canceling the factor $2L+1$ difference between our normalization of A^{μ} and his. Grant's final results [his equations (5.1) and (5.2)] are correct except for the sign of the scalar contribution to the matrix element.

It is also very convenient to define line strengths for the length gauge, since these are, in the nonrelativistic limit, independent of the energy of the transition. One defines the length line strength $S(J_i, J_f)$ by

$$S(J_i,J_f)=\frac{3c^2R}{2\hbar\omega^3}\left|(J_f||\sum h_{\omega 11}(j)||J_i)_L\right|^2 \rightarrow e^2\left|\langle J_f||\sum r_j||J_i\rangle\right|^2 . \quad (34)$$

By studying this quantity, we can measure the effects of relativity on the matrix elements of the length transition operator separately from the relativistic effects on the transition energy.

We also define a momentum strength, $P(J_i, J_f)$, for the velocity form of the dipole transition, which in the nonrelativistic limit is energy independent, and is equal to the square of the matrix element of the momentum:

$$P(J_i,J_f)=\frac{3m^2c^2R}{2e^2\hbar\omega}\left|(J_f||\sum h_{\omega 11}(j)||J_i)_V\right|^2 \rightarrow \left|\langle J_f||\sum P_j||J_i\rangle\right|^2 . \quad (35)$$

Consideration of this quantity enables us to see how the momentum operator is changed by relativity by separating off the energy dependence which appears in the oscillator strength.

The dipole oscillator strength in the length gauge can be expressed in terms of S by

$$f_L=(1/[J_i])(2m\omega/3\hbar e^2)S(J_i,J_f), \quad (36)$$

and, in the velocity gauge, in terms of P by

$$f_V=(1/[J_i])(2/3\hbar\omega m)P(J_i,J_f). \quad (37)$$

III. PROCEDURE AND RESULTS

We have calculated both relativistic length and velocity dipole oscillator strengths for numerous elements in the Li and Be isoelectronic sequences. The complete relativistic expressions for these f values, obtained by combining Eqs. (12), (15), (33), and either (24) or (25), were used. Relativistic radial wave functions were obtained using the multiconfiguration DHF program of Desclaux,[17] modified to run on the Sigma 7 computer of the High Energy Physics Group at Johns Hopkins University. Both ground and excited states of each ion under study were obtained by allowing all orbitals to be varied (no frozen core). The resulting small differences between the core orbitals of the ground and excited states were taken into account by including overlap integrals in the calculation of the transition matrix elements. Transition energies include the configuration average of the first-order correction due to the Breit interaction.[17] It must be noted that the Breit interaction is included in our relativistic calculation only as a first-order correction to the energy; it is not included in the calculation of the wave functions. Thus, for example, Table III does not reflect the breakdown of LS coupling in the Be sequence produced by the Breit interaction—in the Pauli limit, by the spin-spin, orbit-orbit, and a part of the spin–other-orbit interactions. What is included in the calculation of the wave functions are the interactions which in the Pauli limit become the spin-orbit and part of the spin–other-orbit interactions. The point-nucleus approximation was used in all calculations.

For comparative purposes, we have also calculated nonrelativistic wave functions using the multiconfiguration Hartree-Fock program MCHF 75 of Froese-Fisher,[18] similarly modified for use on the Sigma 7. Nonrelativistic calculations were performed in a fashion parallel to that used for the relativistic calculations in order to facilitate comparisons.

A. Lithium sequence

We have obtained length and velocity oscillator strengths of the $2s_{1/2}$-$2p_{1/2,3/2}$, $2s_{1/2}$-$3p_{1/2,3/2}$, $2p_{1/2}$-$3d_{3/2}$, and $2p_{3/2}$-$3d_{3/2,5/2}$ transitions in several elements of the Li sequence. Results are shown in Table I; calculated energies were used in all cases. The length results are shown graphically in Fig. 1; on this scale, they are essentially identical to the velocity results. In this and all other figures we have drawn continuous curves by interpolating between calculated values. Also shown in Fig. 1 are our nonrelativistic values for the same transitions obtained by multiplying $Z^2S(^2S\text{-}^2P)$ by the appropriate line factors; our nonrelativistic values are essentially identical (within 3%) to those obtained by Weiss[19] in a similar calculation (no configuration interaction) up to Ne, the heaviest element considered by Weiss. We note that Weiss[19] also did a multiconfiguration calculation involving 45 terms, which improved the agreement between length and velocity forms somewhat. The length form experienced a 2%–3% change due to this increase in the number of configurations, and the velocity form a 3%–5% change.

TABLE I. Relativistic energies and oscillator strengths (length and velocity forms) for the Li sequence. Nonrelativistic values are in parentheses.

Element	Energy (a.u.)		f_L		f_V		Energy (a.u.)	f_L		f_V	
			$2s \rightarrow 2p_{1/2}$					$2s \rightarrow 2p_{3/2}$			
Li	0.0677	(0.0677)	0.255	(0.255)	0.264	(0.262)	0.0677	0.511	(0.510)	0.524	(0.523)
Be^{+1}	0.147	(0.147)	0.171	(0.171)	0.183	(0.180)	0.147	0.343	(0.343)	0.367	(0.360)
B^{+2}	0.223	(0.222)	0.125	(0.125)	0.138	(0.133)	0.223	0.250	(0.250)	0.272	(0.265)
C^{+3}	0.297	(0.296)	0.097	(0.097)	0.107	(0.104)	0.297	0.195	(0.195)	0.215	(0.208)
N^{+4}	0.370	(0.369)	0.079	(0.080)	0.088	(0.085)	0.371	0.160	(0.159)	0.177	(0.170)
O^{+5}	0.443	(0.441)	0.067	(0.067)	0.075	(0.072)	0.445	0.135	(0.134)	0.151	(0.144)
F^{+6}	0.516	(0.513)	0.058	(0.058)	0.065	(0.062)	0.520	0.118	(0.116)	0.132	(0.124)
Ne^{+7}	0.589	(0.585)	0.051	(0.051)	0.058	(0.055)	0.596	0.104	(0.102)	0.117	(0.109)
Ar^{+15}	1.18	(1.15)	0.026	(0.026)	0.030	(0.027)	1.30	0.058	(0.052)	0.066	(0.054)
Fe^{+23}	1.81	(1.72)	0.018	(0.017)	0.020	(0.017)	2.39	0.048	(0.035)	0.053	(0.035)
Mo^{+39}	3.28	(2.85)	0.011	(0.011)	0.012	(0.010)	7.89	0.056	(0.021)	0.060	(0.019)
W^{+71}	8.05	(5.12)	0.0071	(0.0059)	0.0066	(0.0043)	63.2	0.129	(0.012)	0.131	(0.009)
U^{+89}	13.2	(6.39)	0.0062	(0.0047)	0.0053	(0.0030)	166.9	0.200	(0.009)	0.202	(0.006)
			$2s \rightarrow 3p_{1/2}$					$2s \rightarrow 3p_{3/2}$			
Li	0.140	(0.140)	0.001	(0.001)	0.001	(0.001)	0.140	0.002	(0.002)	0.002	(0.002)
Be^{+1}	0.438	(0.438)	0.026	(0.026)	0.024	(0.025)	0.438	0.052	(0.052)	0.049	(0.050)
B^{+2}	0.877	(0.877)	0.049	(0.050)	0.048	(0.048)	0.877	0.099	(0.099)	0.095	(0.096)
C^{+3}	1.46	(1.46)	0.066	(0.066)	0.064	(0.065)	1.46	0.132	(0.133)	0.128	(0.130)
N^{+4}	2.17	(2.17)	0.078	(0.078)	0.076	(0.077)	2.17	0.156	(0.157)	0.152	(0.154)
O^{+5}	3.03	(3.03)	0.087	(0.087)	0.085	(0.086)	3.03	0.174	(0.175)	0.170	(0.172)
F^{+6}	4.03	(4.02)	0.094	(0.094)	0.092	(0.093)	4.03	0.187	(0.189)	0.184	(0.189)
Ne^{+7}	5.17	(5.16)	0.099	(0.100)	0.098	(0.098)	5.17	0.198	(0.199)	0.195	(0.197)
Ar^{+15}	19.4	(19.2)	0.120	(0.121)	0.119	(0.120)	19.4	0.236	(0.241)	0.234	(0.240)
Fe^{+23}	42.7	(42.2)	0.128	(0.128)	0.127	(0.128)	42.9	0.245	(0.257)	0.244	(0.256)
Mo^{+39}	118.8	(114.8)	0.133	(0.135)	0.133	(0.134)	120.2	0.238	(0.270)	0.237	(0.269)
W^{+71}	412.5	(366.7)	0.136	(0.139)	0.136	(0.139)	429.0	0.176	(0.279)	0.176	(0.278)
U^{+89}	696.1	(570.8)	0.135	(0.140)	0.135	(0.140)	742.1	0.121	(0.281)	0.122	(0.280)
			$2p_{1/2}$-$3d_{3/2}$					$2p_{3/2}$-$3d_{3/2}$			
Li	0.0731	(0.0731)	0.654	(0.654)	0.653	(0.653)	0.0731	0.065	(0.065)	0.065	(0.065)
Be^{+1}	0.297	(0.297)	0.642	(0.642)	0.641	(0.640)	0.297	0.064	(0.064)	0.064	(0.064)
B^{+2}	0.667	(0.667)	0.645	(0.645)	0.644	(0.643)	0.667	0.065	(0.065)	0.064	(0.064)
C^{+3}	1.18	(1.18)	0.650	(0.650)	0.649	(0.648)	1.18	0.065	(0.065)	0.065	(0.065)
N^{+4}	1.83	(1.83)	0.655	(0.655)	0.654	(0.653)	1.83	0.066	(0.066)	0.065	(0.065)
O^{+5}	2.63	(2.62)	0.659	(0.660)	0.658	(0.657)	2.62	0.066	(0.066)	0.066	(0.066)
F^{+6}	3.56	(3.56)	0.662	(0.663)	0.661	(0.661)	3.56	0.066	(0.066)	0.066	(0.066)
Ne^{+7}	4.64	(4.63)	0.664	(0.666)	0.666	(0.664)	4.63	0.067	(0.067)	0.066	(0.066)
Ar^{+15}	18.3	(18.2)	0.673	(0.679)	0.672	(0.677)	18.2	0.068	(0.068)	0.068	(0.068)
Fe^{+23}	41.3	(40.7)	0.670	(0.684)	0.671	(0.682)	40.7	0.068	(0.068)	0.068	(0.068)
Mo^{+39}	117.2	(112.3)	0.651	(0.689)	0.653	(0.687)	112.6	0.068	(0.069)	0.068	(0.069)
W^{+71}	421.4	(362.2)	0.568	(0.692)	0.571	(0.690)	366.3	0.066	(0.069)	0.066	(0.069)
U^{+89}	729.3	(565.2)	0.490	(0.692)	0.494	(0.691)	575.7	0.064	(0.069)	0.065	(0.069)
			$2p_{3/2}$-$3d_{5/2}$								
Li	0.0731		0.588	(0.588	0.588	(0.587)					
Be^{+1}	0.297		0.578	(0.578)	0.577	(0.576)					
B^{+2}	0.667		0.580	(0.581)	0.579	(0.579)					
C^{+3}	1.18		0.585	(0.585)	0.584	(0.583)					
N^{+4}	1.83		0.590	(0.590)	0.589	(0.588)					
O^{+5}	2.63		0.593	(0.594)	0.592	(0.592)					
F^{+6}	3.56		0.597	(0.597)	0.595	(0.595)					
Ne^{+7}	4.63		0.599	(0.600)	0.597	(0.598)					
Ar^{+15}	18.2		0.609	(0.611)	0.608	(0.609)					
Fe^{+23}	40.7		0.611	(0.616)	0.611	(0.614)					
Mo^{+39}	113.0		0.607	(0.620)	0.608	(0.618)					
W^{+71}	370.9		0.583	(0.622)	0.585	(0.621)					
U^{+89}	587.3		0.563	(0.623)	0.564	(0.622)					

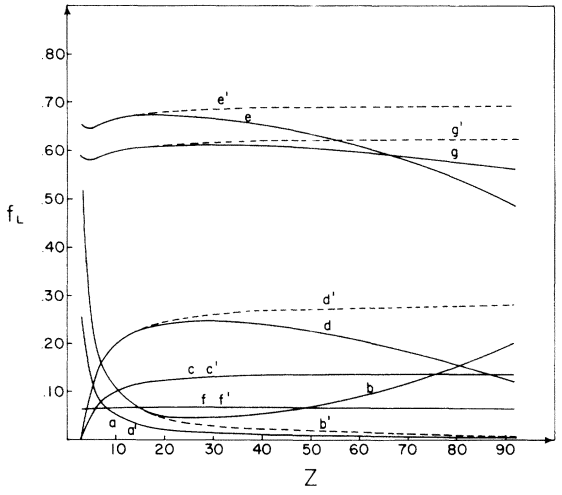

FIG. 1. Length oscillator strengths of the Li I isoelectronic sequence (a) $2s_{1/2}$-$2p_{1/2}$, (b) $2s_{1/2}$-$2p_{3/2}$, (c) $2s_{1/2}$-$3p_{1/2}$, (d) $2s_{1/2}$-$3p_{3/2}$, (e) $2p_{1/2}$-$3d_{3/2}$, (f) $2p_{3/2}$-$3d_{3/2}$, (g) $2p_{3/2}$-$3d_{5/2}$. Prime indicates the nonrelativistic (NR) result.

A recent comparison by Martin and Wiese[20] of experimental and theoretical results for the $2s$-np transitions in the Li sequence shows very good agreement between theory and experiment up to Ne VII, the heaviest atom for which experimental data are available. Our results are also in close agreement with the experimental results insofar as they exist. One sees from Fig. 1 that the relativistic and nonrelativistic values are in good agreement up to about Fe^{23+}, but begin to diverge after that, with the greatest discrepancies occurring in $|\Delta j| = 1$ transitions. We postpone discussion of these and all other results until Sec. IV.

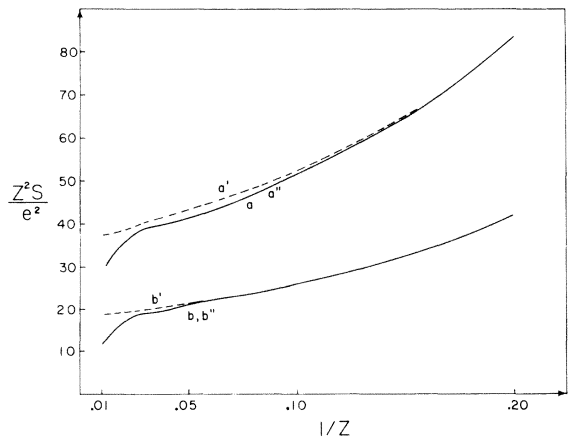

FIG. 2. Z^2S for the Li I isoelectronic sequence (a) $2s_{1/2}$-$2p_{3/2}$, (b) $2s_{1/2}$-$2p_{1/2}$. Prime indicates NR; double prime, the approximate nonrelativistic (ANR) result.

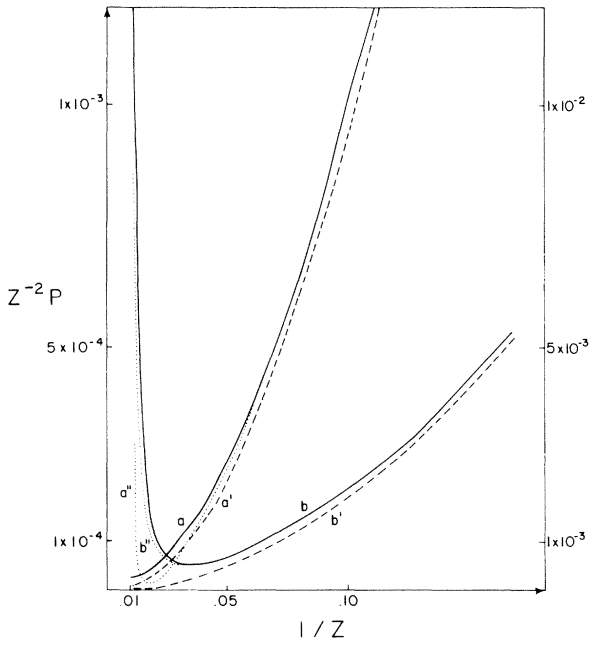

FIG. 3. $Z^{-2}P$ for the Li I isoelectronic sequence. (a) $2s_{1/2}$-$2p_{1/2}$ (left-hand scale), (b) $2s_{1/2}$-$2p_{3/2}$ (right-hand scale). Prime indicates NR; double prime, ANR.

In order to separate relativistic changes in transition energies from the relativistic changes in the matrix elements, we show in Figs. 2–7 plots of Z^2S [Eq. (34)] and $Z^{-2}P$ [Eq. (35)] for the above transitions in the Li isoelectronic sequence, as well as curves calculated using the nonrelativistic limits of Z^2S [Z^2S(NR)] and $Z^{-2}P$ [$Z^{-2}P$(NR)]. The corresponding relativistic and nonrelativistic transition energies are given in Table I.

The nonrelativistic $1/Z$ expansion theory can also be used to predict transition energies and

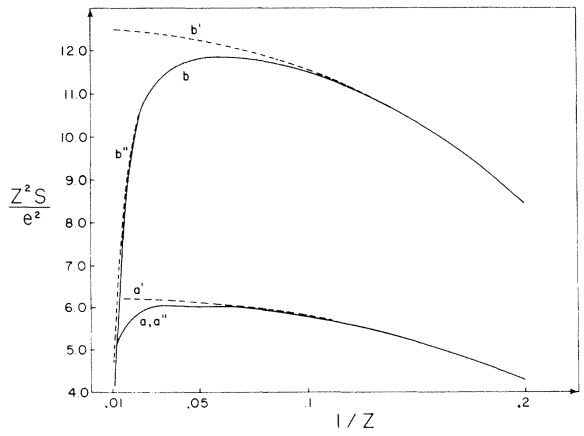

FIG. 4. Z^2S for the Li I isoelectronic sequence (a) $2s_{1/2}$-$3p_{1/2}$, (b) $2s_{1/2}$-$3p_{3/2}$. Prime indicates NR; double prime, ANR.

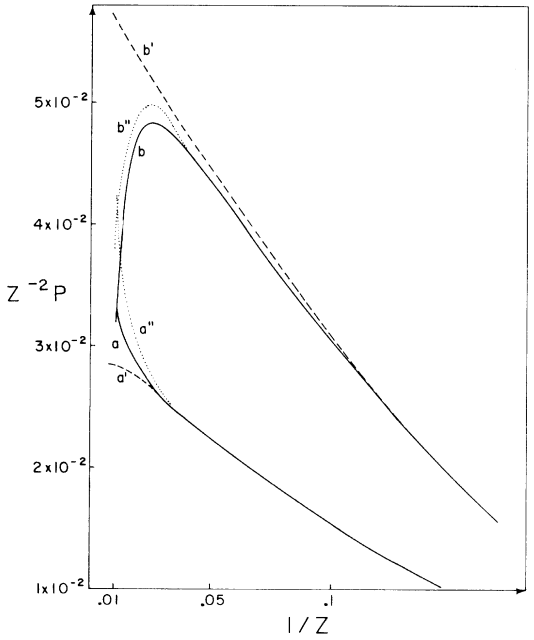

FIG. 5. $Z^{-2}P$ for the Li I isoelectronic sequence (a) $2s_{1/2}$-$^3p_{1/2}$, (b) $2s_{1/2}$-$3p_{3/2}$. Prime indicates NR; double prime, ANR.

oscillator strengths in the Li sequence. Onello *et al.*[21] have studied the $2s\,^2S$-$2p\,^2P$ transition, and found the first eight terms in the energy expansion and first ten terms in the expansion of the oscillator strength. Their results for the energy and f_L

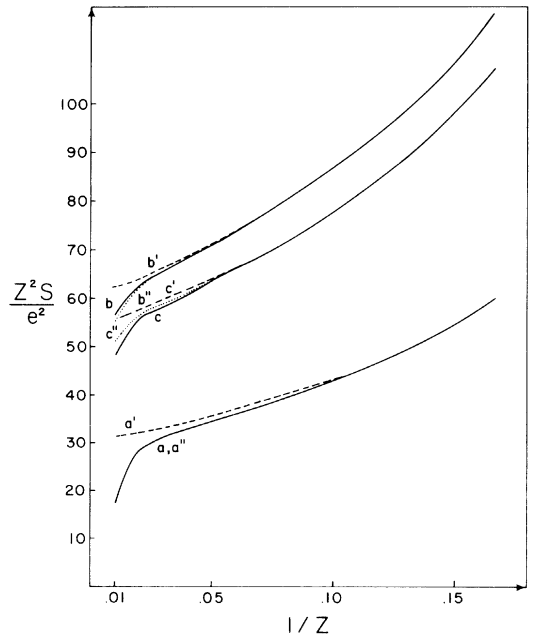

FIG. 6. Z^2S for the Li I isoelectronic sequence (a) $2p_{1/2}$-$3d_{3/2}$, (b) $2p_{3/2}$-$3d_{3/2}$, (c) $2p_{3/2}$-$3d_{5/2}$. Prime indicates NR; double prime, ANR.

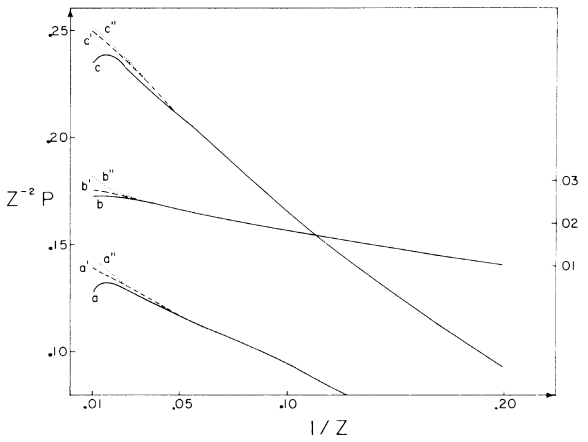

FIG. 7. $Z^{-2}P$ for the Li I isoelectronic sequence (a) $2p_{1/2}$-$3d_{3/2}$ (left-hand scale), (b) $2p_{3/2}$-$3d_{3/2}$ (right-hand scale), (c) $2p_{3/2}$-$3d_{5/2}$ (left-hand scale). Prime indicates NR; double prime, ANR.

agree very well with our nonrelativistic results over the range $5 \leq Z \leq 92$, although there are some small differences between their f_V and ours. Comparison of our nonrelativistic and relativistic results gives therefore an indication of the regions of utility of this $1/Z$ expansion. Clearly, relativistic effects will become important in the transition energy of the $2s_{1/2}$-$2p_{3/2}$ transition about $Z = 15$, and in the energy of the $2s_{1/2}$-$2p_{1/2}$ transition about $Z = 27$. However, the matrix elements used in calculating the f's should be good until about $Z = 30$.

The prediction of the transition energy can be improved considerably using the relativistic $1/Z$ expansion theory. Doyle[22] finds that the $2s_{1/2}$-$2p_{1/2}$ transition energy can be expressed in the form

$$\Delta E_R(\text{a.u.}) = \Delta E_{\text{NR}} + 0.108\,67\alpha^2 Z^3 , \tag{38}$$

and the $2s_{1/2}$-$2p_{3/2}$ transition energy in the form

$$\Delta E_R(\text{a.u.}) = \Delta E_{\text{NR}} + 0.031\,25\alpha^2 Z^4 - 0.109\,435\alpha^3 Z^2 . \tag{39}$$

Comparison of transitions energies obtained using these equations with our relativistic values shows that Eq. (38) is relatively accurate up to about $Z = 50$, and Eq. (39) is accurate up to about $Z = 40$.

Onello[23] and Laughlin *et al.*[24] have studied the $2s$-$3p$ and $2p$-$3d$ transitions using a $1/Z$ theory. Again, these results are in very close agreement with our nonrelativistic results for $5 \leq Z \leq 92$, with the results of Onello[23] being in somewhat better agreement than those of Laughlin *et al.*[24] Again, comparison of our relativistic and nonrelativistic results will give an indication of the range of utility of the $1/Z$ expansion. The onset of relativity

is delayed considerably in these cases, but the nonrelativistic $1/Z$ theory should be reasonably accurate percentagewise until roughly $Z=30-40$.

A simple method for taking relativistic effects into account in an approximate way is to let the nonrelativistic operator act on the large component of the relativistic wave function. In order to find the regions of validity of such an approach, we have also carried approximate nonrelativistic (ANR) length and velocity calculations in which we evaluate the matrix elements

$$\int F_{nlj}\, r\, F_{n'l'j'}\, dr,$$

$$\int F_{nlj}\left(\frac{d}{dr}-\frac{l(l+1)-l'(l'+1)}{2r}\right)F_{n'l'j'}\, dr,$$

respectively. These are then used to evaluate the approximate nonrelativistic values Z^2S(ANR) and $Z^{-2}P$(ANR), which are also shown in Figs. 2–7. One finds that Z^2S and Z^2S(ANR) are in fairly good agreement for all values of Z, differing by only about 7% at the heaviest element considered, U^{+89}. As we discuss below, the results of Kim and Desclaux[4] are, to a good approximation, reproduced by our length ANR results. This work of Kim and Desclaux has also been discussed by Martin and Wiese.[20] Because the ANR calculations are such a good approximation to the complete calculation, many of the conclusions drawn by Kim and Desclaux[4] and Martin and Wiese[20] are identical to our own conclusions. For $|\Delta j|=1$ transitions, $Z^{-2}P$ and $Z^{-2}P$(ANR) are seen to be in fair agreement over the range of Z, but in not so good agreement as seen in the corresponding length matrix elements. For $\Delta j=0$ transitions, on the other hand, $Z^{-2}P$(ANR) is seen to diverge strongly from the correct value given by $Z^{-2}P$ at large values of Z.

Finally, we have evaluated the effective transition operators for the Li sequence using the equations of Sec. II C. Sample values obtained for the $2s$-$2p$ transitions are given in Table II as an indication of the type of effect one observes in the Li sequence. Because of angular momentum selection rules, the only additional operator for the $2s$-np transitions is $A_{11}W^{(11)1}$. The coefficient A_{11} is seen to be negligible for small Z [of the order of $(Z\alpha)^2A^1_{01}$], but to increase in size with increasing Z, roughly as $(Z\alpha)^2$. This increase reflects the increasing relativistic nature of the wave function of the optical electron. Similar results are obtained for the $2s$-$3p$ transitions. For the $2p$-$3d$ transitions, one finds that the coefficients of A^1_{11} and A^1_{12} remain small all the way up to U^{+89}.

TABLE II. Effective length operators of the Li sequence $[A^{K'}_{Kk}=A^K_{Kk}/ie(\hbar\omega/R)^{1/2}]$. $X(Y)$ means $X\times10^Y$.

Element	$2s$-$2p$ $A^{1'}_{01}(2s,2p)$	$2s$-$2p$ $A^{1'}_{11}(2s,2p)$
Li	1.36(−3)	3.86(−7)
F^{+6}	1.80(−3)	8.11(−6)
Ar^{+15}	1.94(−3)	8.76(−5)
Fe^{+23}	2.27(−3)	2.91(−4)
Mo^{+39}	3.91(−3)	1.36(−3)
W^{+71}	1.47(−2)	8.67(−3)
U^{+89}	2.91(−2)	1.85(−2)

B. Beryllium sequences

We have calculated the same types of quantities for the Be sequence as for the Li sequence. The only transitions studied in this case were $2s^2\,{}^1S_0$-$2s2p\,{}^{1,3}P_1$. Both ground and excited states were evaluated using multiconfiguration calculations in the relativistic case: the ground state was taken to be of the form $[(2s_{1/2})^2+(2p_{1/2})^2+(2p_{3/2})^2]J=0$, and the excited state was given by $[2s_{1/2}2p_{1/2}+2s_{1/2}2p_{3/2}]J=1$. The eigenvectors obtained for ground and excited states are shown in Table III. We also give in Table III the eigenvectors expressed in LS notation, in order to make the progression of the breakdown of LS coupling more obvious. In the nonrelativistic case, the ground state was taken to be of the form $(2s^2+2p^2)\,{}^1S_0$ and the single-excited state was given simply by $(2s2p)\,{}^1P_1$.

The resulting relativistic and nonrelativistic f values are tabulated in Table IV; the length form is plotted in Fig. 8. For the ${}^1S_0$-${}^1P_1$ transition, one sees that the relativistic and nonrelativistic curves are quite similar until about Ar^{+14}, at which point they begin to pull apart. The agreement between length and velocity forms for $Z<17$ is slightly better in the relativistic case than in the nonrelativistic case. The length curve starts out higher than the velocity curve, but drops below it around Ne in both relativistic and nonrelativistic calculations. The oscillator strength for the ${}^1S_0$-${}^3P_1$ transition rises after $Z=20$ until reaching a broad flat region between $50<Z<75$. For even higher Z, there is a slight decline in the oscillator strength for this transition.

As mentioned in Sec. I, we have not attempted to do a sophisticated correlation calculation of these oscillator strengths, preferring instead to concentrate on the relativistic aspects of our work. Some comments should be made, however, concerning the effects of configurations not included in our calculation. We give, in Table V, the results of several rather more sophisticated calculations of nonrelativistic length oscillator

TABLE III. Eigenvectors of the Be sequence.

Element	Ground state $^1S_0$ $(2s_{1/2})^2$	$(2p_{1/2})^2$	$(2p_{3/2})^2$	Upper excited state $J=1$ $(2s2p_{1/2})$	$(2s2p_{3/2})$	NR $^1P_1$	NR $^3P_1$
B^{+1}	0.957	0.167	0.237	−0.577	0.817	1.000	0.000
C^{+2}	0.961	0.160	0.226	−0.577	0.817	1.000	0.000
N^{+3}	0.964	0.155	0.218	−0.576	0.817	0.999	0.004
O^{+4}	0.965	0.151	0.213	−0.575	0.818	0.999	0.004
F^{+5}	0.967	0.149	0.209	−0.574	0.819	0.999	0.004
Ne^{+6}	0.968	0.146	0.205	−0.572	0.820	0.999	0.004
Ar^{+14}	0.973	0.140	0.183	−0.533	0.846	0.998	0.006
Fe^{+22}	0.978	0.139	0.155	−0.439	0.898	0.986	0.167
Kr^{+32}	0.984	0.141	0.113	−0.280	0.960	0.945	0.327
Mo^{+38}	0.986	0.141	0.089	−0.200	0.980	0.915	0.403
Xe^{+50}	0.989	0.138	0.054	−0.102	0.995	0.871	0.491
Gd^{+60}	0.991	0.132	0.036	−0.061	0.998	0.850	0.527
W^{+70}	0.992	0.124	0.024	−0.038	0.999	0.837	0.547
Pb^{+78}	0.993	0.116	0.018	−0.027	1.000	0.832	0.555
U^{+88}	0.995	0.104	0.013	−0.018	1.000	0.826	0.564

strengths for the first few members of the Be sequence, as well as our own nonrelativistic results. Our length results are almost identical to those obtained by Burke *et al.*[5] using seven ground configurations and six excited configurations, but not including correlations in the $1s^2$ shell. The main effect of correlation in the calculation of Burke *et al.*[5] was to bring length and velocity curves somewhat closer together than in our calculation, but not to shift the overall curves significantly. The calculation of Nicolaides *et al.*[25] was made using the NCMET theory, and includes some correlations not considered by Burke *et al.*[5]; however, $1s^2$ correlations are still not included. The work of Banyard and Taylor[26] does include $1s^2$ correlations. This correlation is seen to cause a further decrease in the calculated f values. The decrease is only about 4% compared to our results by OV, however, with the agreement between the two calculations increasing with in-

TABLE IV. Relativistic energies and oscillator strengths (length and velocity) for Be sequences. Nonrelativistic values are in parentheses.

Element	$^1S_0$-$^1P_1$ (upper P_1) Energy (a.u.)	f_L	f_V	$^1S_0$-$^3P_1$ (lower P_1) Energy (a.u.)	f_L	f_V
B^{+1}	0.3838 (0.3835)	1.069 (1.065)	0.867 (0.864)	0.1765 (0.1762)	$<10^{-8}$	$<10^{-8}$
C^{+2}	0.5204 (0.5198)	0.791 (0.793)	0.680 (0.672)	0.2457 (0.2452)	$<10^{-7}$	$<10^{-7}$
N^{+3}	0.6522 (0.6507)	0.631 (0.633)	0.573 (0.563)	0.3141 (0.3130)	$<10^{-7}$	$<10^{-7}$
O^{+4}	0.7821 (0.7793)	0.527 (0.527)	0.499 (0.487)	0.3820 (0.3801)	$<10^{-6}$	$<10^{-6}$
F^{+5}	0.9112 (0.9064)	0.452 (0.452)	0.444 (0.430)	0.4497 (0.4467)	$<10^{-6}$	$<10^{-6}$
Ne^{+6}	1.040 (1.033)	0.397 (0.395)	0.401 (0.386)	0.5176 (0.5129)	$<10^{-6}$	$<10^{-6}$
Ar^{+14}	2.128 (2.031)	0.209 (0.198)	0.240 (0.211)	1.088 (1.037)	2.2×10^{-4}	3.0×10^{-4}
Fe^{+22}	3.504 (3.022)	0.156 (0.132)	0.190 (0.144)	1.755 (1.558)	0.0015	0.0024
Kr^{+32}	6.363 (4.259)	0.137 (0.093)	0.171 (0.101)	2.754 (2.208)	0.0054	0.0089
Mo^{+38}	9.260 (5.000)	0.140 (0.079)	0.172 (0.085)	3.427 (2.598)	0.0075	0.0127
Xe^{+50}	19.82 (6.483)	0.168 (0.061)	0.193 (0.064)	4.958 (3.377)	0.0096	0.0158
Gd^{+60}	36.47 (7.718)	0.209 (0.051)	0.231 (0.052)	6.520 (4.026)	0.0099	0.0157
W^{+70}	64.78 (8.953)	0.265 (0.044)	0.284 (0.044)	8.491 (4.674)	0.0099	0.0150
Pb^{+78}	100.1 (9.941)	0.320 (0.040)	0.339 (0.039)	10.50 (5.194)	0.0098	0.0143
U^{+88}	168.1 (11.18)	0.403 (0.035)	0.421 (0.033)	13.82 (5.842)	0.0097	0.0136

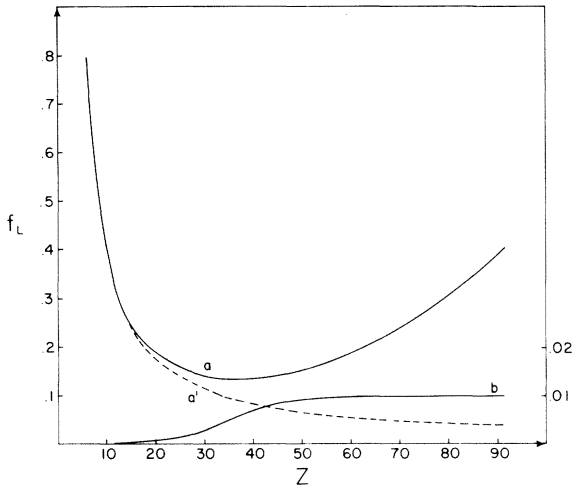

FIG. 8. Length oscillator strengths for the Be I isoelectronic sequence (a) $^1S_0$-$^1P_1$ (left-hand scale), (b) $^1S_0$-$^3P_1$ (right-hand scale). Prime indicates NR.

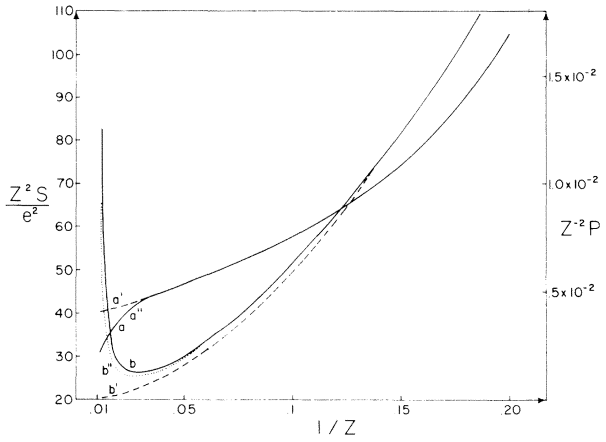

FIG. 9. Line and momentum strengths for the $^1S_0$-$^1P_1$ transition in the Be isoelectronic sequence, (a) Z^2S/e^2 (left-hand scale) (b) $Z^{-2}P$ (right-hand scale). Prime indicates NR; double prime, ANR.

creasing Z. Thus the effects of additional correlation terms on the oscillator strength would appear to be relatively insignificant, particularly at higher Z. However, it should be noted that the available experimental values are even lower than the values of Banyard and Taylor.[26] The origin of this discrepancy is not known, but might be related either to cascading in the beam-foil experiments or to correlations of a type not yet considered.

The transition energies for the various ions under consideration are given in Table IV. In Figs. 9 and 10, we have plotted Z^2S and $Z^{-2}P$ for these transitions. It is obvious that there is no region in which either of these curves can be approximated well by a straight line; a $1/Z$ expansion in this case would thus obviously require that more than the first two terms be kept. This is, in fact, in agreement with the results obtained by Watson and ONeil[27] in their $1/Z$ study of the Be sequence. They obtained the first ten terms in the expansions of the energy and of the line and momentum strengths. For the line strength, the coefficient of the third term in the series, the Z^{-2} term, is, for example, ten times as large as the constant term and therefore obviously not negligible until very large Z. The values of ΔE and f_L obtained by Watson and ONeil[27] are in good agreement with our nonrelativistic results over the range $5 \leq Z \leq 92$; their values of f_V are somewhat higher than ours over the entire range.

We have also shown in Figs. 9 and 10 the approximate forms Z^2S(ANR) and $Z^{-2}P$(ANR). Once again, Z^2S(ANR) is a very good approximation to Z^2S over the entire range of Z. The deviation between the two is only about 3% for U^{+88}. Significant differences are once again obvious between

TABLE V. Nonrelativistic length oscillator strengths.

Element \ Reference	26	25	5	Present work
B^+	0.968	1.00	1.048	1.065
C^{2+}	0.734	0.760	0.793	0.793
N^{3+}	0.596	0.605	0.629	0.633
O^{4+}	0.504	0.513	0.525	0.527
F^{5+}		0.435	0.449	0.452
Ne^{6+}		0.384	0.393	0.395

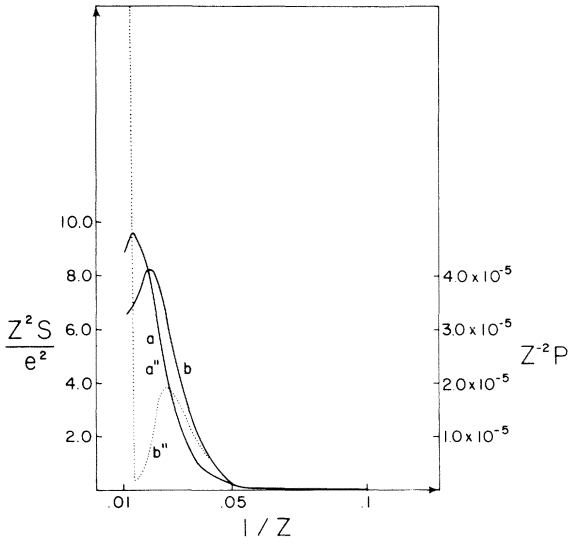

FIG. 10. Line and momentum strengths for the $^1S_0$-$^3P_1$ transition in the Be isoelectronic sequence (a) Z^2S/e^2 (left-hand scale), (b) $Z^{-2}P$ (right-hand scale). Double prime indicates ANR.

TABLE VI. Effective length operators of the Be sequence $[A^{K'}_{\kappa k} = A^{K}_{\kappa k}/ie(\hbar\omega/R)^{1/2}]$. $X(Y)$ means $X\times 10^{Y}$.

Element	$A^{1'}_{01}(2s, 2p)$	$A^{1'}_{11}(2s, 2p)$
B^{+1}	3.37(−3)	1.25(−7)
F^{+5}	3.31(−3)	1.08(−6)
Ar^{+14}	3.36(−3)	5.95(−6)
Fe^{+22}	3.67(−3)	1.47(−5)
Mo^{+38}	5.72(−3)	6.50(−5)
W^{+70}	2.09(−2)	8.36(−4)
U^{+88}	4.08(−2)	2.78(−3)

$Z^{-2}P$(ANR) and $Z^{-2}P$, this time beginning at about Ar^{+14}.

We give in Table VI the values of the effective transition operators $A^1_{01}(ps)$ and $A^1_{11}(ps)$ for this case. As expected, A_{11} is very small for low states of ionization, but begins to grow with increasing ionization, roughly as $(Z\alpha)^2$. The operator A_{11} is very pertinent in this case, since even in the absence of breakdown of LS coupling the operator $A_{11}W^{(11)1}$ could cause the transition $^1S_0$-$^3P_1$. This is a direct demonstration that relativity breaks down the usual LS selection rules for dipole transitions.

IV. DISCUSSION AND CONCLUSIONS

Several conclusions can be drawn from the results presented in Sec. III. The most obvious of these is that one cannot make a single general statement which defines where and when relativistic effects will be important in these two sequences. However, one can make a number of less ambitious statements relating the onset of relativistic effects to such quantities as the Δj and Δn of the transition.

For example, one sees the onset of relativistic effects in the line and momentum strengths for $|\Delta j| = 1, |\Delta n| = 1$ transitions much before they become significant for the $\Delta j = 0, |\Delta n| = 1$ transitions. The converse is true for the $\Delta n = 0$ transitions. One can combine both statements in the rule that relativistic effects on the line strength are stronger in $|\Delta j| = |\Delta n|$ transitions than in transitions for which $|\Delta j| \neq |\Delta n|$—at least for cases in which $|\Delta n| = 0$ or 1. This effect is essentially a one-electron phenomenon in that it is the same as one finds for a relativistic hydrogenlike ion.[28]

One also finds that the energy of the $\Delta n = 0, |\Delta j| = 1$ transition shows a much stronger relativistic effect than does the energy of the $\Delta n = 0, \Delta j = 0$ transition. This effect can be easily understood using a simple $1/Z$ expansion of the energy. The main part of the $2s$-$2p$ transition energy arises from the Coulomb interaction between electrons in the atom, and thus has an expansion of the form $\Delta E = ZE_1 + E_0 + \cdots$. The leading term in the relativistic contribution to this expansion can be obtained by looking at energy separations in the relativistic hydrogen atom. The $2s_{1/2}$ and $2p_{3/2}$ hydrogenic states differ in energy by an amount whose $Z\alpha$ dependence is, in lowest order, the same as that of the spin-orbit interaction, i.e., as $Z^4\alpha^2$. On the other hand, the $2s_{1/2}$ and $2p_{1/2}$ are degenerate for hydrogen, and so there will be no $Z^4\alpha^2$ contribution to their energy separation in a more complex atom. Thus the relativistic effects will be more important for the $|\Delta j| = 1, \Delta n = 0$ transition energies than for the $\Delta j = 0, \Delta n = 0$ ones. This argument is, of course, the basis for the results of Eqs. (38) and (39).

Switching our attention to a comparison of transition energies for transitions having an n change with those not having an n change, one sees that relativity plays a much greater role proportionally in the $\Delta n = 0$ transitions, especially when $|\Delta j| = 1$. This is also easily understood by considering the leading terms in a relativistic $1/Z$ expansion of the transition energy. For $\Delta n = 0$, $|\Delta j| = 1$, the energy expansion has the form

$$\Delta E^0 = ZE_1 + \cdots + Z^4\alpha^2 E_r + \cdots = Z(E_1 + Z^3\alpha^2 E_r + \cdots),$$

whereas the transition energy for a $|\Delta n| = 1, \Delta j = 1$, transition can be expanded as

$$\Delta E^1 = Z^2 E_2 + \cdots + Z^4\alpha^2 E_r + \cdots = Z^2(E_2 + Z^2\alpha^2 E_r + \cdots).$$

Obviously, the relative importance of the relativistic correction increases more rapidly for the former case than for the latter. Since the relativistic effect on the line strength is a $(Z\alpha)^2$ correction, one sees that the relativistic effects on the transition energy have a stronger Z dependence than the relativistic effects on the line strength for $\Delta n = 0, |\Delta j| = 1$ transitions, but the same Z dependence for $|\Delta n| = 1, |\Delta j| = 1$ transitions. One sees, in fact, that for the $2s_{1/2}$-$3p_{3/2}$ transition, relativity produces significant changes in the line strength at a much lower value of Z than the value at which it produces changes in the transition energy.

One rather surprising result is that the ANR calculations of line strength agree so well with the completely relativistic calculation. This is surprising because a number of effects of relative order $(Z\alpha)^2$ are neglected by the ANR calculation. For example, one has kept only the first term, kr, in the expansion of the Bessel functions which appear in the complete operator. This is equivalent to neglecting retardation. The next term in the Bessel function is $(kr)^3$, which for

$\Delta n \neq 0$ transitions should be of the order of $(Z\alpha)^2(kr)$. One has also neglected the small components in evaluating the ANR terms; these also contribute effects of relative order $(Z\alpha)^2$. We have also evaluated the ANR line strengths keeping the small components, i.e., by evaluating

$$\int (F_1F_2 + G_1G_2) r\, dr\,,$$

and found essentially no difference between this value and those obtained using our previously defined ANR operator. Use of this radial integral leads to one of the approximations suggested by Babushkin.[12] This form was used, for example, by Kim and Desclaux[4,29] in their investigation of the Li and Be sequences, and by Younger and Weiss[28] in their study of the H sequence. Because of the lack of importance of the small components in the cases considered here, our ANR length results are essentially identical to the results of Kim and Desclaux.[4] Thus for the line-strength calculation the only important relativistic effect comes in the relativistic shift of the large components, again an effect of relative order $(Z\alpha)^2$, rather than in a change of the form of the transition operator or in the introduction of the small component of the wave function. This indicates the lack of reliability which should be attached to arguments which imply that all terms of a given order in $Z\alpha$ will have roughly the same importance.

The difference between $Z^{-2}P$ and $Z^{-2}P$(ANR) at high values of Z has an interesting origin. In order to investigate this effect, we have looked at the corresponding calculation in a hydrogenic ion, where one can see that this type of discrepancy is caused by a $(Z\alpha)^2$ correction to the momentum operator itself. The small component of the wave function can, of course, be exactly related to the large by

$$G_{nlj} = -\frac{\hbar c}{mc^2 + E - Ze^2/r}\left(\frac{d}{dr} + \frac{\kappa}{r}\right) F_{nlj}\,.$$

One usually approximates this by discarding $-Ze^2/r$ and replacing E by mc^2 in the denominator. Such an approximation used in Eq. (25) leads to the usual momentum form of the dipole operator. However, for highly relativistic ions, the electrons penetrate very close to the nucleus, and the term $-Ze^2/r$ becomes quite large. In such cases this term should be kept, which leads to a $(Z\alpha)^2$ correction to the momentum operator. This correction accounts for the difference between $Z^{-2}P$ and $Z^{-2}P$(ANR). Thus one sees that in the length form, replacing the correct operator by the nonrelativistic operator introduces very little error; in the velocity form, such a replacement may cause considerable error at high Z. This result can probably be generalized to say that in cases in which the relativistic operator is even, i.e., in which it acts between large components, etc., a good approximation to the relativistic result is obtained by simply letting the nonrelativistic operator act between the large components. On the other hand, in cases for which the relativistic operator is odd, i.e., for which it connects large and small components, the same approximation will probably fail at high Z.

As mentioned above, the transition $^1S_0$-$^3P_1$ can be produced by two different effects—the breakdown of LS coupling (Table III), and the relativistic change in the effective LS form of the dipole operator, which is indicated by the magnitude of the operator $A^1_{11}W^{(11)1}(ps)$ (Table VI). The former reflects a sort of "collective relativistic effect" which involves the coupling of all the electrons together under the combined influences of spin-orbit and Coulomb interactions. The latter is an "individual relativistic effect" in that its existence depends on the relativistic nature of the individual electrons. Both effects are of relative order $(Z\alpha)^2$. It can easily be shown that in the present case these two effects make contributions to the transition amplitude of opposite sign, i.e., tend to cancel each other. However, as can be seen by comparing Tables III and VI, it is the breakdown of LS coupling which determines the strength of the $^1S_0$-$^3P_1$ transition until very high Z, where the spin-orbit effect has almost "saturated," that is, pure jj coupling has been reached. On the other hand, the relativistic change in the dipole operator, which is originally of considerably less importance than the spin-orbit effect, continues to grow with increasing Z. As a result, at higher Z there is an increasing cancellation between the two effects, and a corresponding decrease in the line strength.

Younger and Weiss[28] have conjectured that relativistic effects on line strengths might be reasonably taken into account for an ion of nuclear charge Z by multiplying the nonrelativistic line strength by the ratio S_R/S_{NR}, where S_{NR} and S_R are, respectively, the nonrelativistic and relativistic line strengths for a hydrogenic ion of nuclear charge Z. This suggestion seems to be completely supported by the present results, as can be seen by using their results[28] for S_R/S_{NR} in conjunction with our relativistic and nonrelativistic results.

Two more results should be noted. First, the importance of ground-state correlations in the Be sequence decreases with increasing Z, as indicated in Table IV. This result has already been discussed by Kim and Desclaux.[4] Second, one

can claim a slight preference for the nonrelativistic length form of the dipole operator over the nonrelativistic velocity form, since the length form seems to be slightly more insensitive to relativistic effects.

The Li and Be sequences have been chosen for study here because in these cases there is almost no core, and one expects to see results which can, for the most part, be explained using only slight variations on the hydrogenic model. These expectations seem to be borne out, as indicated in the discussion above. In future works, we plan to investigate the effects of a larger core in order to see which, if any, of the results noted here are of a general nature, and which will be limited to systems which are very hydrogenlike.

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