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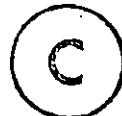
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APPLICATION OF DISCRETE BASIS SET METHODS
TO THE DIRAC EQUATION

by



Samuel Pedro Goldman

A Dissertation
submitted to the Faculty of Graduate Studies
through the Department of
Physics in Partial Fulfillment
of the requirements for the Degree
of Doctor of Philosophy at
The University of Windsor

Windsor, Ontario, Canada

1981

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TO MY PARENTS, SHEINDL AND TSUDYK

APPLICATION OF DISCRETE BASIS SET METHODS

TO THE DIRAC EQUATION

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ABSTRACT

A variational discrete representation of the relativistic energy spectrum of an electron in a Coulomb field is constructed. It is shown that by a proper choice of the variational basis set, the eigenvalues satisfy a generalized Hylleraas-Undheim theorem. A number of relativistic sum rules which can be evaluated exactly are calculated by means of the basis set to demonstrate that the variational solutions obtained by the diagonalization of the Dirac Hamiltonian with a Coulomb potential yield a discrete representation of the hydrogenic spectrum including both the positive and negative continua. The results strongly suggest that the set of relativistic variational eigenvectors and eigenvalues can be used to construct a discrete representation of the Dirac-Green's function.

As applications, the relativistic basis set is used to calculate relativistic values for dipole polarizabilities, electric dipole oscillator strength sums for the ground state with and without retardation, and two-photon decay rates for the metastable $2s_{\frac{1}{2}}$ state in hydrogenic ions. The two-photon decay rates differ from previous calculations due to the inclusion of higher order retardation corrections. Our oscillator strength sums from the ground state appear to be much more accurate than earlier calculations. The oscillator strength densities in the continuum are used to calculate photoionization cross-sections by a Stieltjes imaging technique.

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CHAPTER I

INTRODUCTION

The Variational Method

In non-relativistic quantum mechanics, the variational approach to the eigenvalue problem is well known. In this approach the Schrödinger equation is regarded as the Euler-Lagrange equation for a variational problem where a variation of

$$\langle H \rangle = \int \psi^* H \psi d\tau$$

must be stationary, with the subsidiary normalization condition

$$\int \psi^* \psi = 1.$$

Labeling by E a Lagrangian Multiplier, the solutions of the problem are those that make zero a variation of

$$S = \int \mathcal{L} d\tau$$

with

$$\mathcal{L} = \frac{\hbar^2}{2m} (\nabla \psi^*) (\nabla \psi) + V \psi^* \psi - E \psi^* \psi$$

If ψ and ψ^* are varied independently, the Lagrange equations yield:

$$\frac{\partial \mathcal{L}}{\partial \psi^*} - \sum_k \frac{d}{dx_k} \frac{\partial \mathcal{L}}{\partial \psi^* \partial x_k} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi - E \psi = 0$$

and similarly varying ψ we obtain the same equation for ψ^* .

We note that the Lagrange Multiplier E can be identified with the

expectation value of the energy. It can be shown¹ that it has a lower bound equal to the exact solution E_{exact} . Then, an absolute minimum of $\langle H \rangle$ will yield always an upper bound to the ground state.²

In practice, one chooses a trial function $\psi(\vec{r}, \alpha_i)$ where the α_i 's are variational parameters, and one looks for the values α_i^m of the α_i 's that will satisfy

$$\left. \frac{\partial \langle H \rangle}{\partial \alpha_i} \right|_{\alpha_i^m} = 0.$$

Let now $\{\alpha_i; i=1, 2, \dots, N\}$ denote a set of linear parameters, (i.e., $\psi(\alpha_1 + \alpha_2) = \psi(\alpha_1) + \psi(\alpha_2)$) and β_i a set of non-linear parameters. Being linear parameters, the α_i span a vector space \mathcal{V} which is a subspace of the Hilbert space of exact solutions to H .

If we call P the projector over \mathcal{V} , and by H_p the projected Hamiltonian

$$H_p = P H P,$$

we notice that by construction H_p is hermitian, and

$$H_p \psi \in \mathcal{V}.$$

We can then apply the variational analysis of the preceding paragraphs to conclude that

$$\delta_{\alpha_i} \langle \psi | H_p | \psi \rangle = 0$$

) is equivalent to the eigenvalue problem in \mathcal{V} :

$$H_p \psi = E \psi.$$

The conclusion is then, that the variational solution to an eigenvalue problem where the trial function depends linearly on variational parameters, is given by the diagonalization of the Hamiltonian in the subspace spanned by these parameters.

The solution will contain N eigenvalues (where N is the dimension of \mathcal{V}), the lowest being an upper bound to the ground state, the second lowest to the first excited state and so on, provided that H is a positive-definite operator.

If there are also non-linear parameters β_i , the procedure consists in diagonalizing H_p for different values of the β_i 's until a minimum is obtained.

We will say that \mathcal{V}_N is a complete variational representation of \mathcal{H} , with $\dim[\mathcal{V}_N] = N$ if:

$$\forall \psi \in \mathcal{H}, \quad \psi \in \mathcal{V}_N.$$

For example, in the non-relativistic case, the subspace spanned by vectors of the form

$$\varphi_n = e^{-\lambda r} r^n, \quad n \geq 0$$

where n is an integer, forms a complete representation of the space of hydrogenic wavefunctions.

In this work we attempt a generalization of this procedure to find variational solutions to the Dirac Hamiltonian for one-electron atoms.

In this case the existence of a lower bound is not obvious because the Dirac Hamiltonian H_D contains positive energy solutions, representing

the bound states and the continuum of electron scattering states, and also a continuum of negative energy solutions without a lower bound. Thus, H_D is not a positive-definite operator.

However, for a special family of trial functions, one can obtain a variational representation of both positive and negative energy states. The dimension N of the subspace \mathcal{V}_N^D is always even, and as one increases N , the eigenvalues appear by pairs, one positive and one negative. The positive are upper bounds to the exact solutions and the negative are lower bounds to $-mc^2$.

Although for the one-electron case the exact solutions to the Dirac Hamiltonian are known, a variational representation of these solutions is very important for calculations involving the Green's operator:

$$G_D = \frac{1}{H_D - a} \quad (1.1)$$

or, more generally, hermitian operators of the type:

$$\Lambda = \Omega^\dagger (H_D - a)^k \Omega, \quad (1.2)$$

where Ω is an arbitrary operator.

In the latter case, the expectation value of Λ is

$$\begin{aligned} \langle \psi | \Lambda | \psi \rangle &= \langle \psi | \Omega^\dagger (H_D - a)^k \Omega | \psi \rangle = \\ &= \sum_{n,m} \langle \psi | \Omega^\dagger | \varphi_n \rangle \langle \varphi_n | (H_D - a)^k | \varphi_m \rangle \langle \varphi_m | \Omega | \psi \rangle \end{aligned} \quad (1.3)$$

where the φ_n are a complete set of eigenfunctions of the Hamiltonian, and \sum denotes sum over discrete states and integration over both the positive and negative continua.

We can rewrite the last equation as:

$$\langle \psi | \Lambda | \psi \rangle = \sum_n (E_n - a)^k |\langle \psi | \Omega | \varphi_n \rangle|^2. \quad (1.4)$$

In a variational representation,

$$\langle \psi | \Lambda | \psi \rangle = \sum_{j=1}^N (E_j^{\text{var}} - a)^k |\langle \psi | \Omega | \varphi_j^{\text{var}} \rangle|^2 + E_N, \quad (1.5)$$

where the sum is performed over the vectors of the finite variational subspace, and

$$E_N \xrightarrow[N \rightarrow \infty]{} 0. \quad (1.6)$$

In the non-relativistic case, the variational summation over intermediate states has been widely used.^{3,4}

In the relativistic case, expectation values of the type $\langle \psi | \Lambda | \psi \rangle$ are more difficult to calculate exactly. Different methods have been used to approach the problem: by obtaining the relativistic corrections to the non-relativistic expectation values,⁵ the expansion of the Green's function⁶ or by direct numerical integration of the Green's function.⁷ In our variational procedure, the φ_j^{var} 's are known, and after a calculation of the overlaps $\langle \psi | \Omega | \varphi_j^{\text{var}} \rangle$, a finite sum leads to $\langle \psi | \Lambda | \psi \rangle$.

Chapter I ends with a brief summary of the exact solutions to the Dirac Hamiltonian. In chapters II and III we introduce the relativistic variational wavefunctions, showing that the bound requirements are satisfied. In chapter IV we calculate the electric-dipole relativistic sum rules without retardation (i.e., $\langle \psi | \Lambda | \psi \rangle$ for $\Omega = \vec{r}$). These results are used in chapter V to test the completeness requirements of

the variational representation. In chapter VI we present the relativistic results for electric-dipole polarizability, two-photon decay and the photoeffect.

The Dirac Equation for an Electron

In the presence of an external electromagnetic field, the Dirac equation is:

$$[-ic\hbar\vec{\alpha} \cdot (\nabla - \frac{ie}{\hbar c} \vec{A}) + eA_0 + \beta mc^2] \psi = i\hbar \frac{\partial \psi}{\partial t}$$

or

$$[c\vec{\alpha} \cdot (\vec{p} - \frac{e}{c} \vec{A}) + eA_0 + \beta mc^2] \psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (1.7)$$

For static external fields, stationary solutions exist of the form

$$\psi(\vec{x}, t) = \psi(\vec{x}, t) e^{-i\frac{Et}{\hbar}}, \quad (1.8)$$

$\psi(\vec{x})$ satisfies the eigenvalue equation

$$H_d \psi = E \psi, \quad (1.9)$$

with

$$H_d = c\vec{\alpha} \cdot (\vec{p} - \frac{e}{c} \vec{A}) + eA_0 + \beta mc^2, \quad (1.10)$$

where

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.11)$$

and the $\vec{\sigma}$'s are the standard 2×2 Pauli matrices.

The wave function ψ is a four-component vector or bispinor:

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \quad (1.12)$$

and (1.9) is then a system of four coupled first order differential equations on the functions $\psi_i(x)$.

In the case of a static central potential, (1.10) reduces to:

$$H = c \vec{\alpha} \cdot \vec{p} + V(r) + \beta mc^2. \quad (1.13)$$

The solutions to (1.13) can be written as:⁸

$$\psi_{jLM} = \begin{pmatrix} i \frac{g(r)}{r} \Omega_{jLM}^{(A)} \\ - \frac{f(r)}{r} \Omega_{jLM}^{(A)} \end{pmatrix} \quad (1.14)$$

where l is the orbital angular momentum quantum number, j is the total angular momentum quantum number, $\tilde{l} = 2j-l$, $M=M_j$, f and g are functions of $r=|\vec{r}|$ and Ω_{jLM} is the spherical spinor defined by

$$\Omega_{jLM} = \sum_{m_\mu} \langle l m \frac{1}{2} \mu | j M \rangle Y_{lm}(\hat{r}) \chi^\mu, \quad (1.15)$$

where χ^μ are the basic unit spinors: $\chi^\mu(\lambda) = \delta_{\mu\lambda}$.

The coupled equations satisfied by the radial functions are then:

$$\hbar c \frac{dg}{dr} + \hbar c \frac{K}{r} g - (E - V(r) + mc^2) f = 0 \quad (1.16)$$

$$\hbar c \frac{df}{dr} - \hbar c \frac{K}{r} f + (E - V(r) - mc^2) g = 0,$$

where

$$K = -(l+1) \text{ for } j=l+\frac{1}{2}$$

$$K = l \quad \text{for } j=l-\frac{1}{2} . \quad (1.17)$$

In the case of a Coulomb field, i.e.,

$$V(r) = -\frac{Z e^2}{r} \quad (1.18)$$

system (1.16) becomes

$$\hbar c \frac{dg}{dr} + \hbar c \frac{K}{r} g - \left(E + \frac{Ze^2}{r} + mc^2 \right) f = 0 \quad (1.19)$$

$$\hbar c \frac{df}{dr} - \hbar c \frac{K}{r} f + \left(E + \frac{Ze^2}{r} - mc^2 \right) g = 0$$

or, in atomic units:

$$\frac{dg}{dr} + \frac{K}{r} g - \left(\alpha E + \frac{\alpha Z}{r} + \frac{1}{\alpha} \right) f = 0 \quad (1.20)$$

$$\frac{df}{dr} - \frac{K}{r} f + \left(\alpha E + \frac{\alpha Z}{r} - \frac{1}{\alpha} \right) g = 0 .$$

The eigenvalues to system (1.20) are⁹ for the discrete spectrum,
i.e., $0 < E < mc^2$,

$$E = mc^2 \left[1 + \frac{(\alpha Z)^2}{(n-k + [k^2 - \alpha^2 Z^2]^{1/2})^2} \right]^{-1/2} \quad (1.21)$$

where

$$k = |K| = j + \frac{1}{2}$$

$$n = n' + k \quad \text{with} \quad n' = 0, 1, 2, \dots \quad \text{for} \quad K = -(l+1)$$

$$n' = 1, 2, \dots \quad \text{for} \quad K = l$$

$$\text{and} \quad \alpha = 1/137.03602.$$

We note in (1.21) the explicit degeneracy of E with respect to K .

The eigenfunctions for the discrete spectrum are:

$$g = A \left(1 + \frac{E}{mc^2}\right)^{\frac{1}{2}} e^{-\frac{Z}{Na_0}r} r^\gamma (h_1 - h_2) \quad (1.22)$$

$$f = A \left(1 - \frac{E}{mc^2}\right)^{\frac{1}{2}} e^{-\frac{Z}{Na_0}r} r^\gamma (h_1 + h_2)$$

with

$$A = -\frac{[\Gamma(2\gamma + n' + 1)]^{1/2}}{\Gamma(2\gamma + 1)\sqrt{n'!}} \cdot \frac{1}{4N(N-K)} \left(\frac{2Z}{Na_0}\right)^{\gamma+1}$$

$$N = [n^2 - 2n'(k-\gamma)]^{1/2}$$

$$a_0 = \frac{\hbar}{mc\alpha_{fs}}$$

$$\gamma = [K^2 - \alpha^2 Z^2]^{1/2}$$

$$h_1 = n' F(-n'+1, 2\gamma + 1; \frac{2Zr}{Na_0})$$

$$h_2 = (N-k) F(-n', 2\gamma + 1; \frac{2Zr}{Na_0})$$

The normalization condition for the bound state eigenfunctions, reduces to

$$\int_0^\infty (g^2 + f^2) dr = 1. \quad (1.23)$$

Some general integral properties of the hydrogenic bound state eigenfunctions are presented in Appendix A.

CHAPTER II
THE RELATIVISTIC BASIS SET

In this chapter we introduce the variational basis set that will span the subspace \mathcal{V}_D of solutions to the one-electron problem and calculate the matrix elements of the projected Hamiltonian H_p .

The Variational Basis Set

We try variational solutions of the form:

$$\psi_{var} = e^{-\lambda r} r^{\gamma-1} \sum_{n=0}^N \left\{ a_n r^n \begin{pmatrix} i \Omega_{jLM} \\ 0 \end{pmatrix} + b_n r^n \begin{pmatrix} 0 \\ -\Omega_{jLM} \end{pmatrix} \right\} \quad (2.1)$$

where the a_n , b_n are linear variational parameters and λ , γ are non-linear variational parameters, all of them varied in order to minimize an expectation value of the Hamiltonian.

For a given value of λ and γ , the problem of finding the stationary solutions of

$$E(\psi_{var}) = \frac{\langle \psi_{var} | H | \psi_{var} \rangle}{\langle \psi_{var} | \psi_{var} \rangle} \quad (2.2)$$

is, as discussed in Chapter I, equivalent to finding the eigenvalues of the projected Hamiltonian:

$$(P H P) \psi = E \psi \quad (2.3)$$

where P is the projector into the Hilbert space \mathcal{H}_p spanned by the basis vectors:

$$\begin{aligned} \psi_{j\ell M}^{(p)} &= i \frac{\zeta^{(p)}}{r} \begin{pmatrix} \Omega_{j\ell M} \\ 0 \end{pmatrix} \\ \omega_{j\ell M}^{(p)} &= -\frac{\zeta^{(p)}}{r} \begin{pmatrix} 0 \\ \Omega_{j\ell M} \end{pmatrix} \end{aligned} \quad (2.4)$$

with

$$\tilde{\ell} = 2j - \ell,$$

$$\zeta^{(p)}(r) = e^{-\lambda r} r^{\gamma+p} \quad p=0, 1, 2, \dots$$

In other words, the problem is reduced to the matrix diagonalization of $\langle \phi_i | H | \phi_j \rangle$ where the ϕ_i 's are independent vectors in \mathcal{H}_p .

Using

$$\int \Omega_{j\ell M}^\dagger \Omega_{j'\ell' M'} d\omega = \delta_{jj'} \delta_{\ell\ell'} \delta_{MM'} \quad (2.5)$$

and

$$\int_0^\infty e^{-\alpha r} r^\beta dr = \frac{\Gamma(\beta+1)}{\alpha^{\beta+1}} \quad (2.6)$$

we obtain:

$$\langle \psi_{j\ell M}^{(p)} | \psi_{j'\ell' M'}^{(p')} \rangle = \langle \omega_{j\ell M}^{(p)} | \omega_{j'\ell' M'}^{(p')} \rangle = N(p, p') \delta_{jj'} \delta_{\ell\ell'} \delta_{MM'} \quad (2.7)$$

and

$$\langle \psi_{j\ell M}^{(p)} | \psi_{j'\ell' M'}^{(p')} \rangle = 0, \quad (2.8)$$

the last equation being a consequence of spinor orthogonality, and

$$N(p, p') = N(p', p) = \frac{\Gamma(2\gamma + p + p' + 1)}{(2\lambda)^{(2\gamma + p + p' + 1)}}. \quad (2.9)$$

Defining

$$\omega(p, p') = \frac{N(p, p')}{[N(p, p) N(p', p')]^{1/2}} = \frac{\Gamma(2\gamma + p + p' + 1)}{[\Gamma(2\gamma + 2p + 1) \Gamma(2\gamma + 2p' + 1)]^{1/2}} \quad (2.10)$$

we can now avoid the large values of Γ occurring in (2.7) by defining the normalized basis vectors:

$$\hat{\psi}_{j\ell M}^{(p)} = \frac{1}{\sqrt{N(p,p)}} \left(\begin{array}{c} \zeta^{(p)} \\ \vdots \\ \Omega_{j\ell M} \\ 0 \end{array} \right) \quad (2.11)$$

$$\hat{\omega}_{j\ell M}^{(p)} = \frac{-1}{\sqrt{N(p,p)}} \left(\begin{array}{c} \zeta^{(p)} \\ \vdots \\ 0 \\ \Omega_{j\ell M} \end{array} \right)$$

with

$$\zeta^{(p)} = e^{-\lambda r} r^{\gamma+p} \quad p=0,1,2,\dots$$

$$N(p,p) = \frac{\Gamma(2\gamma+2p+1)}{\lambda^{(2\gamma+2p+1)}},$$

with these definitions,

$$\langle \hat{\psi}_{j\ell M}^{(p)} | \hat{\psi}_{j'\ell' M'}^{(p')} \rangle = \langle \hat{\omega}_{j\ell M}^{(p)} | \hat{\omega}_{j'\ell' M'}^{(p')} \rangle = \delta_{jj'} \delta_{\ell\ell'} \delta_{MM'} \omega(p,p'). \quad (2.12)$$

For computational purposes, calling

$$n = |\rho - \rho'|$$

$$2\tilde{\nu} = 2\gamma + 2[\max(\rho, \rho')],$$

(2.10) becomes

$$\omega(\rho, \rho') = 1 \quad \text{if } p=p'$$

$$\omega(\rho, \rho') = \begin{cases} \frac{(2\tilde{\nu}-n)(2\tilde{\nu}-n-1)\dots(2\tilde{\nu}-2n+1)}{2\tilde{\nu}(2\tilde{\nu}-1)\dots(2\tilde{\nu}-n+1)}^{\frac{1}{2}} & \text{if } p \neq p' \\ \text{if } p=p' \end{cases} \quad (2.13)$$

Orthonormalization

Because of the condition

$$\langle \hat{v}_{j \in M}^{(p)} | \hat{w}_{j' \in M'}^{(p')} \rangle = 0$$

the overlap matrix consists automatically of two irreducible parts, and because of (2.12) those two parts are identical and equal to $\omega(p,p')$.

The orthonormal basis set will consist then of the vectors

$$\begin{aligned} V^{(q)} &= \sum_p v_{pq} \hat{v}^{(q)} \\ W^{(q)} &= \sum_p v_{pq} \hat{w}^{(q)} \end{aligned} \tag{2.14}$$

where the coefficients v_{pq} are the same in both cases.

The task of orthonormalization is reduced then to the diagonalization of $\omega(p,p')$. (Note that $\omega(p,p')$ contains half the number of rows and columns as the overlap matrix)

Call U_{ij} the transformation matrix such that

$$U_{ik} \omega(k,k') U_{k'j} = \gamma_{ij} \delta_{ij}. \tag{2.15}$$

Then in (2.14)

$$v_{pq} = \frac{U_{pq}}{\gamma_{qq}}$$

The Hamiltonian Matrix Elements

We note from (1.8) that the eigenvalue problem is reduced to the solution of

$$H_r \xi = E \xi \quad (2.16)$$

where

$$\xi = \begin{pmatrix} g \\ f \end{pmatrix} \quad (2.17)$$

with g and f defined in (1.6), and

$$H_r = \hbar c (-i \tilde{\sigma}_y) \frac{d}{dr} + \hbar c \frac{1}{r} \tilde{\sigma}_x + mc^2 \tilde{\sigma}_z - \frac{ze^2}{r} \quad (2.18)$$

where the $\tilde{\sigma}_i$'s are the standard Pauli spin matrices.

Again, the variational problem of finding the wavefunctions that will make a variation of $\langle \xi | H_r | \xi \rangle$ stationary is equivalent to the diagonalization of H_r in the Hilbert space spanned by the variational basis set.

Calling

$$\phi^{(i)} = V^{(i)} \quad \text{if } j=i; i=0,1,2,\dots,N \quad (2.19)$$

$$\phi^{(i)} = W^{(i)} \quad \text{if } j=i+N; i=0,1,2,\dots,N$$

where N is the maximum value of p in (2.11), the problem is reduced to the diagonalization of

$$\langle \phi^{(i)} | H_r | \phi^{(i)} \rangle .$$

Using now (2.11) and (2.18) we obtain

$$\begin{aligned}
 \langle \hat{\omega}^{(p)} | H | \hat{\omega}^{(p')} \rangle &= \int_0^\infty \left(-\frac{ze^2}{r} + mc^2 \right) \frac{\bar{\gamma}^{(p)} \bar{\gamma}^{(p')}}{\sqrt{N(p,p) N(p',p')}} dr = \\
 &= \frac{1}{\sqrt{N(p,p) N(p',p')}} \left[mc^2 N(p,p) - ze^2 N(p,p'-1) \right] = \\
 &= \omega(p,p') \left\{ mc^2 - \frac{ze^2 \lambda}{\gamma + \frac{1}{2}(p+p')} \right\}. \tag{2.20a}
 \end{aligned}$$

In the same way

$$\langle \hat{\omega}^{(p)} | H | \hat{\omega}^{(p')} \rangle = \omega(p,p') \left\{ -mc^2 - \frac{ze^2 \lambda}{\gamma + \frac{1}{2}(p+p')} \right\} \tag{2.20b}$$

$$\begin{aligned}
 \langle \hat{\omega}^{(p)} | H | \hat{\omega}^{(p')} \rangle &= \int_0^\infty \frac{\bar{\gamma}^{(p)} \hbar c}{\sqrt{N(p,p) N(p',p')}} \left[\frac{d\bar{\gamma}^{(p)}}{dr} + \frac{\kappa}{r} \bar{\gamma}^{(p)} \right] dr = \\
 &= \frac{\hbar c}{\sqrt{N(p,p) N(p',p')}} \left\{ -\lambda N(p,p') + (\gamma + p' + \kappa) N(p,p'-1) \right\} = \\
 &= \hbar c \omega(p,p') \lambda \left\{ -1 + \frac{2(\gamma + p' + \kappa)}{2\gamma + p + p'} \right\} = \\
 &= \hbar c \omega(p,p') \lambda \frac{(p' - p + 2\kappa)}{2\gamma + p + p'} \tag{2.20c}
 \end{aligned}$$

We note that

$$\frac{\langle \hat{w}^{(p)} | H | \hat{w}^{(p')} \rangle}{\langle \hat{w}^{(p)} | H | w^{(p)} \rangle} = \frac{p' - p + 2K}{p - p' + 2K} \quad (2.20d)$$

In atomic units, equations (2.20) become:

$$\langle \hat{w}_{j\ell M}^{(p)} | H | \hat{w}_{j\ell M}^{(p')} \rangle = \omega(p, p') \left\{ \frac{1}{\alpha^2} - \frac{\lambda z}{\gamma + \frac{1}{2}(p+p')} \right\} \quad (2.21a)$$

$$\langle \hat{w}_{j\ell M}^{(p)} | H | w_{j\ell M}^{(p)} \rangle = \omega(p, p') \left\{ -\frac{1}{\alpha^2} - \frac{\lambda z}{\gamma + \frac{1}{2}(p+p')} \right\} \quad (2.21b)$$

$$\langle \hat{w}_{j\ell M}^{(p)} | H | w_{j\ell M}^{(p)} \rangle = \frac{1}{\alpha} \omega(p, p') \frac{\lambda(p' - p + 2K)}{2\gamma + p + p'} , \quad (2.21c)$$

where

$$\omega(p, p') = \frac{\Gamma(2\gamma + p + p' + 1)}{\left[\Gamma(2\gamma + 2p + 1) \Gamma(2\gamma + 2p' + 1) \right]^{1/2}} \quad (2.10)$$

λ and γ are non-linear variational parameters.

For γ was used the exact value

$$\gamma = \sqrt{k^2 - \alpha^2 Z^2} \quad (2.22)$$

which is independent of the energy eigenvalues and defined for a given value of K , as the basis set is. We would then expect this value of γ to be a minimizing one.

The exact value for λ is:

$$\lambda_{\text{exact}} = \frac{1}{\alpha} \left[1 - \alpha^4 E^2 \right]^{1/2} \quad (2.23a)$$

with

$$\alpha^4 E^2 = \left\{ 1 + \frac{(\alpha z)^2}{(n - |K| + [K^2 - \alpha^2 z^2]^{1/2})^2} \right\}^{-1} \quad (2.23b)$$

Then, if λ_{exact} is used for λ in a case in which $n < N$, we will expect, after the diagonalization of the hamiltonian, the n -th level to appear exactly.

CHAPTER III
THE VARIATIONAL ENERGY SPECTRUM

After the calculation of the matrix elements of H_p in the last chapter, we discuss in detail the behaviour of the spectrum of solutions under the variation of the non-linear parameters, and the requirements for the positive-energy solutions to be upper bounds to the exact eigenvalues. It is also seen that half of the eigenvalues will always be negative and lower bounds to $-mc^2$. (The set of negative energy eigenvalues forms a discrete representation of the negative continuum which extends from $-mc^2$ to $-\infty$. In the same way, the positive energy eigenvalues with $E > mc^2$ cover the scattering continuum.)

The Variational Eigenvalues

The diagonalization of

$$\langle \phi^{(i)} | H_r | \phi^{(j)} \rangle$$

with $\phi^{(i)}$ defined in (2.19), yields a discrete spectrum of positive and negative eigenvalues. The number of positive energy eigenvalues equals the number of negative energy eigenvalues, and equals half the dimension of the variational Hilbert space \mathcal{H}_p .

This spectrum provides a discrete synthetic representation of the bound states and both the positive and negative energy continuum spectra for an hydrogenic potential. In other words, it will be shown that for the Green's operator

$$(H - E)^{-1} = \sum_{0 < E_n < mc^2} \frac{|\psi_n\rangle \langle \psi_n|}{E_n - E_0} + \int_{E > mc^2} \frac{|\psi_E\rangle \langle \psi_E|}{E - E_0} \rho_E dE \quad (3.1)$$

$$+ \int_{E \leq mc^2} \frac{|\psi_E\rangle\langle\psi_E|}{E - E_0} \rho_E dE$$

the variational basis set provides a complete representation in the sense

$$(H - E_0)^{-1} = \sum_{n=1}^{2N} \frac{|\phi^{(n)}\rangle\langle\phi^{(n)}|}{E_n - E_0} + \epsilon, \quad (3.2)$$

where ϵ can be made as small as desired by increasing the dimension N.

Figure 1 shows schematically the way in which the $s_{1/2}$ eigenvalues for $Z=92$ appear for progressively larger basis sets. The exponential parameter used is $\lambda = 65.2$, corresponding to a generating level (value of n in λ , equation (2.23)) $n=1.5$.

In Tables 1, 2, and 3 we list as an example, the generated spectra for the $s_{1/2}$, $p_{1/2}$, and $p_{3/2}$ series for $Z=20$. The generating level is 1.5, and the number of basis vectors is 28 (twice 14).

We note the appearance of an extra "1p_{1/2}" level. The reason is that the relativistic wavefunctions for the $K>0$ states use the same value of γ as the $K<0$ counterparts, i.e., unlike the non-relativistic case, the behaviour at the origin is determined by $|K|$ and then the $s_{1/2}$ and $p_{1/2}$ states have the same behaviour for small r. If $N-1$ is the maximum value of p in (2.11), then the number of positive eigenvalues is N for the $K<0$ series and $N-1$ for the $K>0$ series. In the case $K>0$ there remains then an extra eigenvector. This extra wavefunction oscillates rapidly and does not contribute to the sum in (3.2). In our following calculations for sum rules and two-photon emission, no difference could be recorded by the inclusion or omission of this state.

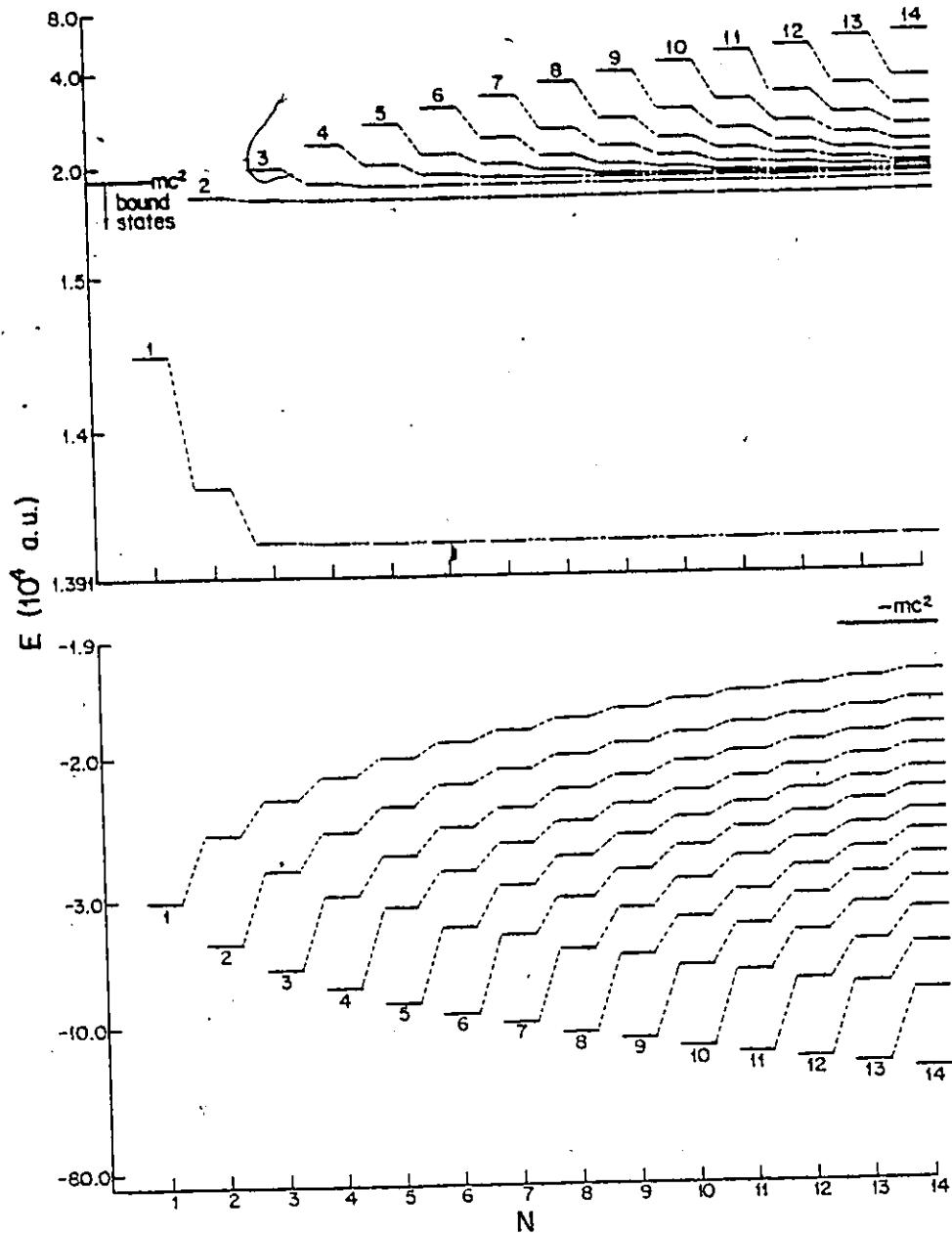


FIGURE 1. Distribution of the $s_{1/2}$ variational eigenvalues for $Z=92$ and $\lambda=65.2$ as a function of the size of the basis set.

TABLE 1

Variational Eigenvalues for $s_{1/2}$ States, Z=20

n	$E_{>0} - mc^2$ (A.U.)	$E_{<0} + mc^2$ (A.U.)
	variational	exact
1	-0.201076522879 (3)	-0.201076522879 (3)
2	-0.503365941134 (2)	-0.503365941134 (2)
3	-0.223417619749 (2)	-0.223417722492 (2)
4	-0.124913235190 (2)	-0.125545908749 (2)
5	-0.610976904075 (1)	-0.802922220132 (1)
6	0.340585067711 (1)	-0.557295585063 (1)
7	0.184992299978 (2)	-0.131556174467 (3)
8	0.420549907474 (2)	-0.185386801949 (3)
9	0.798622511631 (2)	-0.267913573141 (3)
10	0.144336153673 (3)	-0.403338473903 (3)
11	0.265568155242 (3)	-0.648341819690 (3)
12	0.531641038391 (3)	-0.116296582007 (4)
13	0.129206090124 (4)	-0.255780018668 (4)
14	0.502510433758 (4)	-0.903208014914 (4)

TABLE 2

Variational Eigenvalues for $p_{1/2}$ States for Z=20

n	$E_{>0} - mc^2$ (A.U.)	$E_{<0} + mc^2$ (A.U.)
	variational	exact
1	-0.200373891927 (3)	-0.155797434299 (2)
2	-0.503365941135 (2)	-0.503365941134 (2)
3	-0.223417619807 (2)	-0.223417722492 (2)
4	-0.124913452996 (2)	-0.125545908749 (2)
5	-0.611014175393 (1)	-0.802922220132 (1)
6	0.340452409501 (1)	-0.557295585063 (1)
7	0.184959423017 (2)	-0.131464058743 (3)
8	0.420475752169 (2)	-0.185282774138 (3)
9	0.798460526717 (2)	-0.267809877795 (3)
10	0.144301721498 (3)	-0.403258487955 (3)
11	0.265498653030 (3)	-0.648321081717 (3)
12	0.531513072364 (3)	-0.116304495720 (4)
13	0.129185562712 (4)	-0.255800556805 (4)
14	0.502482805509 (4)	-0.903239677427 (4)

TABLE 3

Variational Eigenvalues for $p_{3/2}$ States for Z=20

n	$E_{>0} - mc^2$ (A.U.)	$E_{<0} + mc^2$ (A.U.)
	variational	exact
1	-0.500667419965 (2)	-0.500667419965 (2)
2	-0.222617798539 (2)	-0.222617808531 (2)
3	-0.125021318862 (2)	-0.125208596566 (2)
4	-0.698958132118 (1)	-0.801196016511 (1)
5	0.319004585220	-0.556297035513 (1)
6	0.116295091923 (2)	-0.870352061440 (2)
7	0.285153790780 (2)	-0.119327977170 (2)
8	0.538622457029 (2)	-0.165360189901 (3)
9	0.931429211756 (2)	-0.233905463750 (3)
10	0.157464462038 (3)	-0.342245430284 (3)
11	0.271976841397 (3)	-0.528452405652 (3)
12	0.503586456928 (3)	-0.890803787763 (3)
13	0.108122272357 (4)	-0.175398039572 (4)
14	0.325070921350 (4)	-0.481521678555 (4)

Bounds

A rigorous proof that the positive variational spectrum provides an upper bound on the lowest positive eigenvalue and that the negative variational spectrum provides a lower bound to $-mc^2$ has been found by Drake¹⁰ for the case $N=1$. In this section we analyze the numerical results for $N > 1$, in order to generalize this result to any value of N .

As described in Figure 1 schematically, and as shown in Table 4, it was found that the positive energy eigenvalues provide upper bounds to the bound-state energies in the hydrogenic problem. As can be seen in Table 4, the larger the dimension of the basis set, the closer the variational eigenvalues converge to the exact eigenvalues always from above.

It is interesting to note that this situation is true only for the case in which the subspaces spanned by the functions g or f in (2.17) are identical. It was found that if the number of powers of r in $\tilde{\gamma}^{(p)}$ for the upper and lower components in (2.4) was different, then the variational spectrum would not provide upper bounds to the positive energies.

In other words, it was found that a trial function of the form

$$\psi_{var} = e^{-\lambda r} r^{\gamma-1} \left\{ \sum_{n=0}^{N_1} a_n r^n \begin{pmatrix} i \Omega_{j\ell M} \\ 0 \end{pmatrix} + \sum_{n=0}^{N_2} b_n r^n \begin{pmatrix} 0 \\ -\Omega_{j\ell M} \end{pmatrix} \right\}$$

will yield an upper bound for the ground state only in the case $N_1=N_2$.

In Figure 2 we can observe the behaviour of the positive energy levels as a function of the number of independent lower component vectors. In this case $Z=50$, $N_1=14$, and $2 \leq N_2 \leq 14$.

The set has been found to provide upper bounds also under a variation of the non-linear parameters γ and λ .

Figures 3 and 4 show the γ -dependence of the $2s_{1/2}$ and $2p_{3/2}$ levels

TABLE 4

$s_{1/2}$ Variational Levels for Different

Basis Sets for $Z = 92$

LEVEL	$E_{>0} - mc^2$ (A.U.)				
	N = 1	N = 2	N = 3	N = 4	N = 6
14					
13					
12					
11					
10					
9					
8					
7					
6				9.7546 (3)	
5				2.1914 (3)	
4			5.6050 (3)	2.0343 (2)	
3		9.9822 (2)	-2.1019 (2)	-5.1098 (2)	
2	-1.0779 (3)	-1.2460 (3)	-1.2568 (3)	-1.2574 (3)	
1	-4.5569 (3)	-4.8375 (3)	-4.8600 (3)	-4.8611 (3)	-4.8612 (3)

Table 4 continued

LEVEL	$E_{>0} - mc^2$ (A.U.)				EXACT VALUES
	N = 8	N = 10	N = 12	N = 14	
14				3.7885 (4)	
13				1.6206 (4)	
12			3.0646 (4)	8.5535 (3)	
11			1.2372 (4)	4.8955 (3)	
10		2.5494 (4)	6.1241 (3)	2.8817 (3)	
9		8.6913 (3)	3.2350 (3)	1.6739 (3)	
8	1.6489 (4)	3.8684 (3)	1.6925 (3)	9.0751 (2)	
7	5.2486 (3)	1.7399 (3)	7.9625 (2)	4.0414 (2)	
6	1.8580 (3)	6.5481 (2)	2.4983 (2)	7.0173 (2)	-1.2709 (2)
5	4.6739 (2)	6.0316 (1)	-8.5194 (1)	-1.4484 (2)	-1.8549 (2)
4	-1.7810 (2)	-2.6656 (2)	-2.8894 (2)	-2.9409 (2)	-2.9526 (2)
3	-5.3699 (2)	-5.3898 (2)	-5.3909 (2)	-5.3909 (2)	-5.3909 (2)
2	-1.2574 (3)	-1.2574 (3)	-1.2574 (3)	-1.2574 (3)	-1.2574 (3)
1	-4.8612 (3)	-4.8612 (3)	-4.8612 (3)	-4.8612 (3)	-4.8612 (3)

TABLE 5

$s_{1/2}$ Negative Variational Levels for Different
Basis Sets for $Z = 92$

LEVEL	$E_{<0} + mc^2$ (A.U.)				
	N = 1	N = 2	N = 3	N = 4	N = 6
1	-1.1630 (4)	-4.1302 (3)	-2.3802 (3)	-1.6455 (3)	-9.9248 (2)
2		-2.2328 (4)	-7.2122 (3)	-3.9589 (3)	-1.9488 (3)
3			-3.3854 (4)	-1.0582 (4)	-3.7153 (3)
4				-4.5838 (4)	-7.5001 (3)
5					-1.7992 (4)
6					-7.0493 (4)
7					
8					
9					
10					
11					
12					
13					
14					

Table 5 continued

LEVEL	$E_{<0} + mc^2$ (A.U.)			
	N = 8	N = 10	N = 12	N = 14
1	-7.0018 (2)	-5.3656 (2)	-4.3276 (2)	-3.6138 (2)
2	-1.2472 (3)	-9.0066 (2)	-6.9721 (2)	-5.6466 (2)
3	-2.0965 (3)	-1.4155 (3)	-1.0497 (3)	-8.2466 (2)
4	-3.5116 (3)	-2.1766 (3)	-1.5355 (3)	-1.1669 (3)
5	-6.0911 (3)	-3.3523 (3)	-2.2224 (3)	-1.6248 (3)
6	-1.1496 (4)	-5.2811 (3)	-3.2251 (3)	-2.2493 (3)
7	-2.5987 (4)	-8.7344 (3)	-4.7530 (3)	-3.1216 (3)
8	-9.5593 (4)	-1.5819 (4)	-7.2250 (3)	-4.3803 (3)
9		-3.4331 (4)	-1.1585 (4)	-6.2774 (3)
10		-1.2090 (5)	-2.0375 (4)	-9.3117 (3)
11			-4.2892 (4)	-1.4596 (4)
12			-1.4633 (5)	-2.5096 (4)
13				-5.1593 (4)
14				-1.7183 (5)

respectively for $Z = 50$ using a 6-dimensional (twice) basis set. In both cases a non-minimizing value of λ was used.

As expected, the value of γ that will minimize any level is the exact one. The reason is that the variational vector space \mathcal{H}_p is constructed for a given value of K , i.e., K is the same for all the levels. Since \mathcal{H}_p is a subspace of \mathcal{H} , and since γ is the same for all the vectors in \mathcal{H} , γ must equal γ_{exact} in \mathcal{H}_p too.

Tables 6 and 7 show the λ -dependence of the $2p_{1/2}$ and $2p_{3/2}$ levels respectively for $Z=50$ for a 6-dimensional (twice) and a 14-dimensional (twice) basis set.

With regard to the variational negative energy eigenvalues, as we can see in Table 5, they are a lower bound to $-mc^2$, with each level approaching the $-mc^2$ value from below as the dimension of the basis set is increased.

TABLE 6

The $2p_{\frac{1}{2}}$ State as a Function of
the Exponential Parameter

λ	$E - mc^2$ (A.U.) (N = 6)	$E - mc^2$ (A.U.) (N = 14)	$E - mc^2$ (A.U.) (exact)
10	-315.503	-326.4940	-326.494799458
20	-326.4946998	-326.494799458	
30	-326.494797	-326.494799458	
40	-326.4553	-326.494799458	
50	-325.244	-326.49479883	
60		-326.49467	

TABLE 7
The $2p_{3/2}$ State as a Function of
the Exponential Parameter

λ	$E - mc^2$ (A.U.) (N = 6)	$E - mc^2$ (A.U.) (N = 14)	$E - mc^2$ (A.U.) (exact)
10	-313.139745	-315.144299	-315.144353993
20	-315.144353501	-315.144353993	
30	-315.144353948	-315.144353993	
40	-315.141768	-315.144353993	
50	-314.98771	-315.144353923	
60	-313.71855	-315.144334	

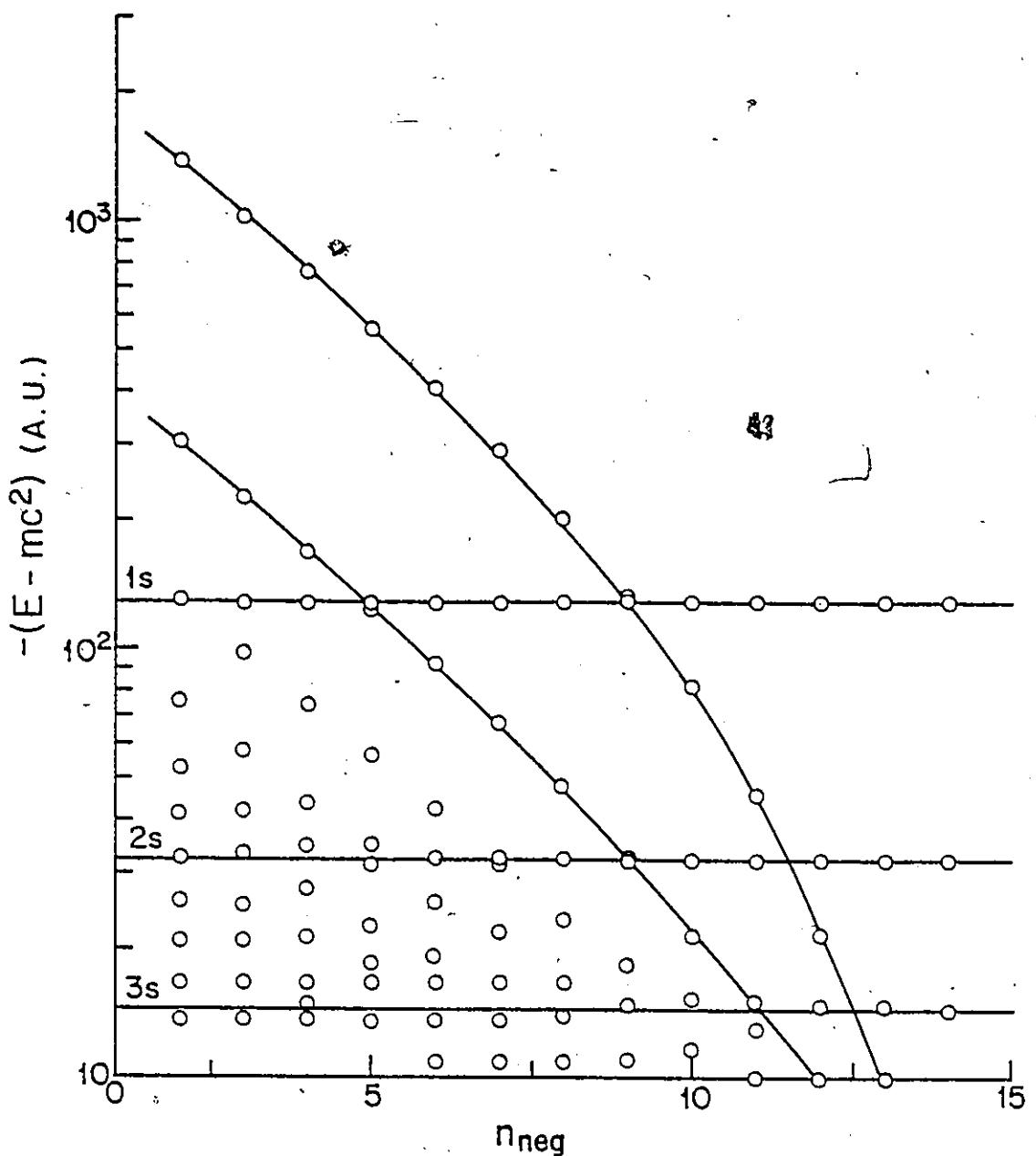


FIGURE 2. Behaviour of the variational positive energy eigenvalues as a function of the number of independent lower component vectors.

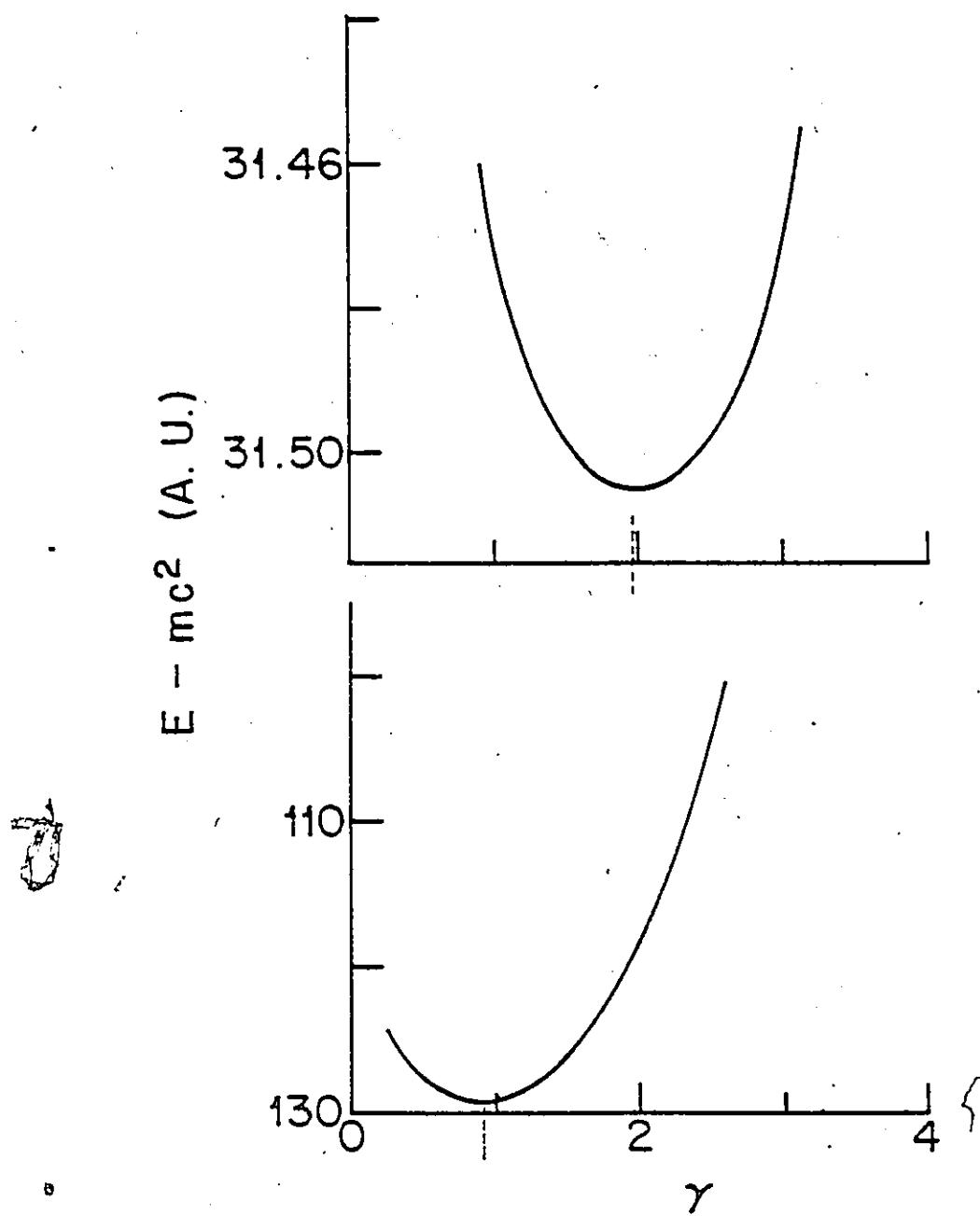


FIGURE 3 (top). γ -dependence of the 2s energy level for $Z=50$, using a 6-dimensional (twice) basis set. The dotted line shows γ_{exact} .

FIGURE 4 (bottom). γ -dependence of the 2p energy level for $Z=50$ using a 6-dimensional (twice) basis set. The dotted line shows γ_{exact} .



CHAPTER IV

SUM RULES

Non-Relativistic Sum Rules

In non-relativistic Quantum Mechanics, sum rules of the type

$$S_k^{NR} = \oint_n (E_n - E_0)^k |\langle \psi_0 | \vec{r} | \psi_n \rangle|^2 \quad (4.1)$$

where \oint denotes sums over discrete levels and integration over the continuum, can be calculated exactly and yield for hydrogenic ions^{11,12} in A.U.:

$$S_0^{NR} = \langle \psi_0 | r^2 | \psi_0 \rangle \quad (4.2a)$$

$$S_1^{NR} = \frac{3}{2} \quad (\text{Thomas-Reiche-Kuhn sum rule}) \quad (4.2b)$$

$$S_2^{NR} = 2 \langle \psi_0 | (E - V) | \psi_0 \rangle \quad (4.2c)$$

$$S_3^{NR} = \frac{1}{2} \langle \psi_0 | (\nabla^2 V) | \psi_0 \rangle \quad (4.2d)$$

The right hand side in equations (4.2) is known exactly, so, by performing the summations in (4.1) explicitly using the variational wave functions, we can test the completeness of the basis set, or the validity of the proposition that the expectation value of

$$(H - \omega)^k - \sum_{n=1}^{2N} |\psi_n^{var}\rangle \langle \psi_n^{var}| (E_n - \omega)^k = \mathcal{E} \quad (4.3)$$

can be made arbitrarily small by increasing the dimension N of the variational basis set.

In the relativistic case, however, the sums (4.1) and (4.3) will include the negative energy states.

We note that while S_0 tests the validity of

$$\sum_n |\psi_n\rangle \langle \psi_n| = 1,$$

higher order sum rules will test how well the basis set synthesizes the information contained in the higher energy continuum states.

Because the variational exponential parameter will always be close to the value of an exponential parameter corresponding to an exact bound state (of finite energy), it is to be expected that the higher the order of the sum rule, the poorer the agreement will be with the exact value for a basis set of a given dimension. However, if the set is complete for $N \rightarrow \infty$, we will still expect the condition $\mathcal{E} \rightarrow 0$ to be satisfied as the dimension N is increased.

For later comparison we might specialize the sum rules (4.2) for the case in which ψ_0 is the non-relativistic wave-function of the ground state for hydrogenic ions. In A.U.

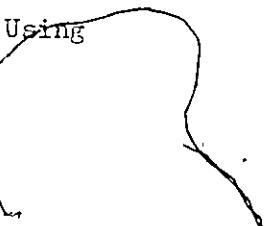
$$\psi_{0NR} = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Zr},$$



(4.4a)

$$E_0 = -Z^2/2$$

(4.4b)



Using

$$\langle r^2 \rangle_o = \frac{3}{Z^2} \quad (4.4c)$$

$$\langle V \rangle_o = \left\langle -\frac{Z}{r} \right\rangle_o = -Z^2 \quad (4.4d)$$

$$\langle \delta(r) \rangle_o = \left(\frac{Z^3}{\pi} \right), \quad (4.4e)$$

we obtain for the ground state:

$$S_o^{NR} = \frac{3}{Z^2} \quad (4.5a)$$

$$S_1^{NR} = \frac{3}{2} \quad (4.5b)$$

$$S_2^{NR} = Z^2 \quad (4.5c)$$

$$S_3^{NR} = 2Z^4 \quad (4.5d)$$

Relativistic Sum Rules Without Retardation

We would like now to find the relativistic equivalents of (4.1), that is:

$$S_k = \sum_n (E_n - E_o)^k \left| \langle \psi_o | \vec{r} | \psi_n \rangle \right|^2 + \\ + \int_{\substack{E > mc^2 \\ E < -mc^2}} \rho_E (E - E_o)^k \left| \langle \psi_o | \vec{r} | \psi_E \rangle \right|^2 dE \quad (4.6)$$

where ρ_E is the density of states. (e.g., the discrete sum is the special case $\rho_E = \sum_n S(E - E_n)$.)

In this section we will find the exact solutions for sums of the type (4.6) and in Chapter V we will compare these results with those obtained by direct evaluation using the variational basis set.

All the evaluations will be done in atomic units, and to avoid confusion we will sometimes use $c = 1/\alpha$ instead of the fine structure α which can be mistaken for $\vec{\alpha}$.

We will denote by ψ_n , ψ , the members of a complete set of solutions to the Dirac Hamiltonian. We will use the notation

$$[\vec{A} * \vec{B}] = \sum_j [A_j, B_j], \quad (4.7)$$

and by

$$\sum_s f(E_s) g(\psi_s),$$

where f and g are arbitrary functions of the arguments, we mean the sum over discrete states and the integration over positive and negative continua. For example:

$$\sum_s |\psi_s\rangle \langle \psi_s| = \sum_{0 < E_n < mc^2} |\psi_n\rangle \langle \psi_n| + \int_{|E| > mc^2} |\psi_E\rangle \langle \psi_E| \rho_E dE = 1. \quad (4.8)$$

Using (4.8), the first sum rule S_0 is obtained:

$$S_0 = \langle \psi_0 | \vec{r} \cdot \left(\sum_s |\psi_s\rangle \langle \psi_s| \right) \vec{r} | \psi_0 \rangle = \langle \psi_0 | r^2 | \psi_0 \rangle \quad (4.9)$$

as in the non-relativistic case, with the difference that now ψ_0 is a bispinor solution to the Dirac equation.

We shall use now the explicit form of the Dirac Hamiltonian for a static radial potential:

$$H = -ic\vec{\alpha} \cdot \nabla + \beta c^2 + V(r) \quad (4.10)$$

and the identities

$$[\vec{r}, H] = -ic[\vec{r}, \vec{\alpha} \cdot \nabla] = ic\vec{\alpha}, \quad (4.11)$$

$$[[\vec{r}, H], * \vec{r}] = ic[\vec{\alpha}, * \vec{r}] = 0. \quad (4.12)$$

To obtain the sum rule S_1 , we write:

$$\begin{aligned} S_1 &= \sum_n (E_n - E_o) \langle \psi_o | \vec{r} | \varphi_n \rangle \cdot \langle \varphi_n | \vec{r} | \psi_o \rangle = \\ &= \sum_n \langle \psi_o | [\vec{r}, H] | \varphi_n \rangle \cdot \langle \varphi_n | \vec{r} | \psi_o \rangle = \\ &= - \sum_n \langle \psi_o | \vec{r} | \varphi_n \rangle \cdot \langle \varphi_n | [\vec{r}, H] | \psi_o \rangle = \\ &= \frac{1}{2} \langle \psi_o | [[\vec{r}, H], * \vec{r}] | \psi_o \rangle = 0 \end{aligned}$$

where we used (4.12). From the last equation

$$S_1 = \sum_n (E_n - E_o) |\langle \psi_o | \vec{r} | \varphi_n \rangle|^2 = 0. \quad (4.13)$$

We note that the sum over negative energy states exactly cancels

the positive energy contribution.¹³ If we limit the sum in (4.13) to the

positive energy levels, we will then obtain the relativistic correction to the Thomas-Reiche-Kuhn sum rule (4.2b).

To obtain S_2 , we write, using (4.11):

$$2 \sum_n (E_n - E_0)^2 |\langle \psi_0 | \vec{F} | \psi_n \rangle|^2 = - \sum_n \langle \psi_0 | [\vec{F}, H] | \psi_n \rangle \cdot \langle \psi_n | [\vec{F}, H] | \psi_0 \rangle = \\ = - \langle \psi_0 | (ic\vec{\alpha})^2 | \psi_0 \rangle = 3C^2.$$

Therefore

$$S_2 = 3C^2. \quad (4.16)$$

Using the results for S_1 and S_2 we can obtain other second order sum rules like:

$$\tilde{S}_2 = \sum_n (E_n^2 - E_0^2) |\langle \psi_0 | \vec{F} | \psi_n \rangle|^2 = S_2 + 2E_0 S_1 = 3C^2. \quad (4.17)$$

We obtain now the third order sum rule S_3 . We note first that:

$$\langle \psi_n | [H, [H, \vec{F}]] | \psi_0 \rangle = \langle \psi_n | H^2 \vec{F} - 2H \vec{F} H + \vec{F} H^2 | \psi_0 \rangle = \\ = (E_n - E_0)^2 \langle \psi_n | \vec{F} | \psi_0 \rangle. \quad (4.18)$$

Then,

$$S_3 = \sum_n (E_n - E_0)^3 |\langle \psi_n | \vec{F} | \psi_0 \rangle|^2 = \\ = \sum_n \langle \psi_0 | [\vec{F}, H] | \psi_n \rangle \cdot \langle \psi_n | [H, [H, \vec{F}]] | \psi_0 \rangle =$$

$$= \langle \psi_0 | A_3 | \psi_0 \rangle , \quad (4.19a)$$

where

$$A_3 = \frac{1}{2} [[\vec{F}, H] * [H, [H, \vec{F}]]] . \quad (4.19b)$$

Using (4.10) and (4.11), the second term in the commutator in A_3 is

$$\begin{aligned} [H, [H, x_j]] &= iC [\alpha_j, H] = iC \left\{ [\alpha_j, (-iC \vec{\alpha} \cdot \nabla)] + C^2 [\alpha_j, \beta] \right\} = \\ &= C^2 \sum_k [\alpha_j, \alpha_k] \partial_k + iC^3 [\alpha_j, \beta] \end{aligned}$$

where

$$\partial_k = \frac{\partial}{\partial x_k} .$$

Using

$$[\alpha_j, \alpha_k] = \sum_n 2i\epsilon_{njk} \tilde{G}_n^D \quad (4.20a)$$

where ϵ_{njk} is the Levi-Civita tensor and

$$\tilde{G}_n^D = \begin{pmatrix} G_n & 0 \\ 0 & G_n \end{pmatrix} \quad (4.20b)$$

and

$$\{ \alpha_j, \beta \} = \alpha_j \beta + \beta \alpha_j = 0 , \quad (4.20c)$$

we obtain

$$[H, [H, x_j]] = \sum_{nk} 2iC^2 \epsilon_{jkn} \tilde{G}_n^D \partial_k + 2iC^3 \alpha_j \beta . \quad (4.21)$$

We use from now on in this section, unless otherwise stated, the convention that a sum is carried over an index that appears twice in a product or a function, i.e.,

$$a_i b_i = \sum_i a_i b_i; f_{ii} = \sum_i f_{ii}.$$

In (4.19b), we obtain

$$\begin{aligned} 2A_3 &= [ic\alpha_j, 2ic^2\epsilon_{jkn}\tilde{\epsilon}_n^3\partial_k] + [ic\alpha_j, 2ic^3\alpha_j\beta] = \\ &= -2c^3[\alpha_j, \tilde{\epsilon}_n^3]\epsilon_{jkn}\partial_k - 2c^4[\alpha_j, \alpha_j]\beta = \\ &= -2c^3[\alpha_j, \tilde{\epsilon}_n^3]\epsilon_{jkn}\partial_k - 2c^4\{\alpha_j, \alpha_j\}\beta. \end{aligned}$$

Using now

$$[\alpha_j, \tilde{\epsilon}_n^3] = 2i\epsilon_{mjn}\alpha_m \quad (4.22a)$$

and

$$\{\alpha_j, \alpha_k\} = 2\delta_{jk} \quad (4.22b)$$

we can write

$$A_3 = -2ic^3\epsilon_{mjn}\epsilon_{jkn}\alpha_m\partial_k - 6c^4\beta.$$

Since

$$\epsilon_{abc}\epsilon_{ade} = \delta_{bd}\delta_{ce} - \delta_{be}\delta_{cd}, \quad (4.22c)$$

$$A_3 = -2ic^3(\delta_{hk}\delta_{mn} - \delta_{nn}\delta_{mk})\alpha_m\partial_k - 6c^4\beta =$$

$$= 4ic^3 \vec{\alpha} \cdot \nabla - 6c^4 \beta.$$

Using (4.10)

$$\beta c^2 = H + ic\vec{\alpha} \cdot \nabla - V.$$

Therefore

$$A_3 = -2ic^3 \vec{\alpha} \cdot \nabla - 6c^2 H + 6c^2 V. \quad (4.23)$$

We note that

$$\begin{aligned} [H, \vec{F} \cdot \nabla] &= -ic\alpha_j [\partial_j, x_k \partial_k] + [V, x_k \partial_k] = \\ &= -ic\alpha_j [\partial_j, x_k] \partial_k + x_k [V, \partial_k] = \\ &= -ic\vec{\alpha} \cdot \nabla - \vec{F} \cdot (\nabla V), \end{aligned} \quad (4.24)$$

and that in the case $V = V(r)$

$$-ic\vec{\alpha} \cdot \nabla = [H, \vec{F} \cdot \nabla] + r \frac{dV}{dr}. \quad (4.25)$$

Using now all these results in (4.19a)

$$S_3 = 2c^2 \langle \psi | [H, \vec{F} \cdot \nabla] / \psi \rangle + 2c^2 \langle \psi | r \frac{dV}{dr} / \psi \rangle -$$

$$-6c^2 \langle \psi | H | \psi \rangle + 6c^2 \langle \psi | V | \psi \rangle.$$

But

$$\langle \psi_0 | [H, \vec{r} \cdot \nabla] | \psi_0 \rangle = 0$$

Since ψ_0 is an eigenvector of H . Then, finally:

$$S_3 = -6c^2 E_0 + 6c^2 \langle \psi_0 | V | \psi_0 \rangle + 2c^2 \langle \psi_0 | r \frac{dV}{dr} | \psi_0 \rangle. \quad (4.26)$$

In the case of an electron in a Coulomb potential $V_C = -\frac{Z}{r}$ and (4.26) becomes:

$$S_3 = -6c^2 E_0 + 4c^2 \langle \psi_0 | V_C | \psi_0 \rangle. \quad (4.27)$$

Using (4.18) we can now proceed to obtain S_4 :

$$\begin{aligned} S_4 &= \sum_n (E_n - E_0)^4 |\langle \psi_0 | \vec{r} | \varphi_n \rangle|^2 = \\ &= \sum_n \langle \psi_0 | [H, [H, \vec{r}]] | \varphi_n \rangle \langle \varphi_n | [H, [H, \vec{r}]] | \psi_0 \rangle = \\ &= \langle \psi_0 | A_4 | \psi_0 \rangle \end{aligned} \quad (4.28a)$$

with

$$A_4 = \frac{1}{2} \left\{ [H, [H, \vec{r}]] * [H, [H, \vec{r}]] \right\} \quad (4.28b)$$

where

$$\{A, B\} = AB + BA$$

Using (4.21):

$$\begin{aligned}
 2A_4 &= \left\{ (2ic^2 \epsilon_{jkn} \tilde{\epsilon}_n^3 \partial_k + 2ic^3 \alpha_j \beta), (2ic^2 \epsilon_{jlm} \tilde{\epsilon}_m^3 \partial_l + 2ic^3 \alpha_j \beta) \right\} = \\
 &= -4c^4 \epsilon_{jkn} \epsilon_{jlm} \left\{ \tilde{\epsilon}_n^3, \tilde{\epsilon}_m^3 \right\} \partial_k \partial_l - 8c^5 \epsilon_{jkn} \left\{ \tilde{\epsilon}_n^3, \alpha_j \beta \right\} \partial_k - \\
 &\quad - 4c^6 \left\{ \alpha_j \beta, \alpha_j \beta \right\}. \tag{4.29}
 \end{aligned}$$

Using now

$$\left\{ \tilde{\epsilon}_n^3, \tilde{\epsilon}_m^3 \right\} = 2 \delta_{nm} \tag{4.30a}$$

$$\left\{ \tilde{\epsilon}_n^3, \alpha_j \beta \right\} = \left\{ \tilde{\epsilon}_n^3, \alpha_j \right\} \beta = 2 \rho \delta_{nj} \beta \tag{4.30b}$$

$$\left\{ \alpha_j \beta, \alpha_j \beta \right\} = - \left\{ \alpha_j, \alpha_j \right\} \tag{4.30c}$$

where

$$\rho = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{4.30d}$$

and

$$\epsilon_{ijk} \delta_{jk} = 0,$$

we obtain

$$\begin{aligned}
 2A_4 &= -4c^4 (\delta_{kl} \delta_{nm} - \delta_{km} \delta_{nl}) 2 \delta_{nm} \partial_k \partial_l - 4c^6 \left\{ \alpha_j, \alpha_j \right\} = \\
 &= -16c^4 \nabla^2 + 24c^6. \tag{4.31}
 \end{aligned}$$

Finally in (4.28a):

$$S_4 = -8c^4 \langle \psi_0 | \nabla^2 | \psi_0 \rangle + 12c^6. \quad (4.32)$$

We proceed now to obtain S_5 . Using (4.10) and (4.21), we calculate first:

$$\begin{aligned} [H, [H, [H, x_j]]] &= 2ic^2 [H, \epsilon_{jkn} \tilde{\epsilon}_n^3 \partial_k] + 2ic^3 [H, \alpha_j \beta] = \\ &= 2c^3 [\alpha_m, \tilde{\epsilon}_n^3] \epsilon_{jkn} \partial_m \partial_k + 2ic^4 [\beta, \tilde{\epsilon}_n^3] \epsilon_{jkn} \partial_k + \\ &\quad + 2ic^2 [V, \partial_k] \epsilon_{jkn} \tilde{\epsilon}_n^3 + 2c^4 [\alpha_m, \alpha_j \beta] \partial_m + \\ &\quad + 2ic^5 [\beta, \alpha_j \beta]. \end{aligned}$$

Using

$$[\alpha_m, \tilde{\epsilon}_n^3] = 2i \epsilon_{omn} \alpha_\ell \quad (4.33a)$$

$$[\beta, \tilde{\epsilon}_n^3] = 0 \quad (4.33b)$$

$$[\alpha_m, \alpha_j \beta] = \{\alpha_m, \alpha_j\} \beta = 2 \delta_{mj} \beta \quad (4.33c)$$

$$[\beta, \alpha_j \beta] = -2 \alpha_j \quad (4.33d)$$

we obtain

$$[H, [H, [H, x_j]]] = 4ic^3 \alpha_j \nabla^2 - 4ic^3 (\vec{\alpha} \cdot \nabla) \partial_j -$$

$$-2ic^2\mathcal{E}_{jkn}\tilde{v}_n^{\mathfrak{D}}V_{jk} + 4c^4\beta\partial_j - 4ic^5\alpha_j. \quad (4.34)$$

We can write the fifth sum rule in the following way:

$$S_5 = \sum_n (E_n - E_0)^5 |\langle \psi_0 | F | \psi_n \rangle|^2 = \langle \psi_0 | A_5 | \psi_0 \rangle \quad (4.35a)$$

with

$$2A_5 = [[H, [H, F]] * [H, [H, [H, F]]]]. \quad (4.35b)$$

We now calculate the operator A_5 using (4.21) and (4.34).

$$\begin{aligned} 2A_5 = & -8c^5[\tilde{v}_n^{\mathfrak{D}}, \alpha_j]\mathcal{E}_{jkn}\partial_k\nabla^2 + 8c^5[\tilde{v}_n^{\mathfrak{D}}, \alpha_k]\mathcal{E}_{jkn}\partial_j\partial_k\partial_\ell + \\ & + 4c^4[\tilde{v}_n^{\mathfrak{D}}\partial_k, \tilde{v}_m^{\mathfrak{D}}V_{jk}]\mathcal{E}_{jkn}\mathcal{E}_{jlm} + 8ic^6[\tilde{v}_n^{\mathfrak{D}}, \beta]\mathcal{E}_{jkn}\partial_k\partial_j + \\ & + 8c^7[\tilde{v}_n^{\mathfrak{D}}, \alpha_j]\mathcal{E}_{jkn}\partial_k - 8c^6[\alpha_j\beta, \alpha_j]\nabla^2 + \\ & + 8c^6[\alpha_j\beta, \alpha_k]\partial_k\partial_j + 4c^5[\alpha_j\beta, \tilde{v}_n^{\mathfrak{D}}]\mathcal{E}_{jkn}V_{jk} + \\ & + 8ic^7[\alpha_j\beta, \beta]\partial_j + 8c^8[\alpha_j\beta, \alpha_j]. \end{aligned}$$

Using

$$\mathcal{E}_{jkn}\partial_j\partial_k = 0$$

and equations (4.33),

$$2A_5 = -32ic^5(\vec{\alpha} \cdot \nabla)\nabla^2 + 4c^4\tilde{v}_n^{\mathfrak{D}}\tilde{v}_m^{\mathfrak{D}}V_{jk}(\delta_{kl}\delta_{nm} - \delta_{km}\delta_{nl}) -$$

$$-8ic^4 \mathcal{E}_{nms} \tilde{v}_s V_n \partial_m + 32ic^7 \vec{\alpha} \cdot \nabla + 32c^6 \beta \nabla^2 -$$

$$-16ic^5 \vec{\alpha} \cdot (\nabla V) \beta + 16ic^7 \vec{\alpha} \cdot \nabla - 48c^8 \beta .$$

We use now

$$\tilde{v}_n^D \tilde{v}_m^D = \delta_{nm} + i\mathcal{E}_{nmb} \tilde{v}_b^D$$

and obtain

$$\tilde{v}_m^D \tilde{v}_m^D \nabla^2 = 3\nabla^2,$$

$$\tilde{v}_n^D \tilde{v}_m^D \partial_n \partial_m = \frac{1}{2} \left\{ \tilde{v}_n^D, \tilde{v}_m^D \right\} \partial_n \partial_m = \nabla^2, \quad (4.36)$$

and

$$\begin{aligned} [H, [H, V]] &= -c^2 (\nabla^2 V) - 2ic^2 \mathcal{E}_{njk} \tilde{v}_n^D V_k \partial_j - \\ &- 2ic^3 \beta \vec{\alpha} \cdot (\nabla V) \end{aligned} \quad (4.37)$$

Calling

$$K = \beta (\vec{v}^D \cdot \vec{L} + \hbar) = \beta (\vec{v}^D \cdot \vec{J} - \frac{\hbar}{2})$$

we note that¹⁴

$$[H, K] = 0$$

and

$$[V_k \partial_k \beta, K] = -i [\beta V_k \partial_k, \beta \tilde{c}_j^D \epsilon_{jmn} x_m \partial_n] = \\ = -i \epsilon_{njk} \tilde{c}_n^D V_j \partial_k + i \epsilon_{njk} \tilde{c}_n^D x_j V_{,lk} \partial_l.$$

But

$$\epsilon_{njk} \tilde{c}_n^D x_j V_{,lk} = \frac{\partial}{\partial x_k} (\tilde{c}_n^D \vec{r} \times (\nabla V)) = 0 \quad \text{for } V = V(r).$$

Therefore

$$[\beta V_k \partial_k, K] = -i \epsilon_{njk} \tilde{c}_n^D V_{,j} \partial_k. \quad (4.38)$$

Using these results:

$$2A_5 = 32 c^4 (-i c \vec{a} \cdot \nabla + \beta c^2) \nabla^2 - 48 c^6 (-i c \vec{a} \cdot \nabla + \beta c^2) + \\ + 8 c^4 [K, \beta(\nabla V) \cdot \nabla] - 8 c^2 [H, [H, V]] \quad (4.39)$$

Then, finally:

$$S_5 = 16 c^4 \langle \psi_o | (E_o - V) \nabla^2 | \psi_o \rangle - 24 c^6 \langle \psi_o | (E_o - V) \nabla^2 | \psi_o \rangle. \quad (4.40)$$

We note that for ψ_o belonging to states with $K=1$ the term $\langle \psi_o | V \nabla^2 | \psi_o \rangle$ diverges.

We obtain then, for the relativistic case, the following sum rules:

$$S_o = \langle \psi_o | r^2 | \psi_o \rangle \quad (4.9)$$

$$S_1 = 0 \quad (4.13)$$

$$S_2 = 3c^2 \quad (4.16)$$

$$S_3 = -4c^2 \langle \psi_0 | \vec{r} \cdot (\nabla V) | \psi_0 \rangle - 6c^4 \langle \psi_0 | \beta | \psi_0 \rangle \quad (4.23)$$

$$S_4 = -8c^4 \langle \psi_0 | \nabla^2 | \psi_0 \rangle + 12c^6 \quad (4.32)$$

$$S_5 = 16c^4 \langle \psi_0 | (E_0 - V) \nabla^2 | \psi_0 \rangle - 24c^6 \langle \psi_0 | (E_0 - V) | \psi_0 \rangle \quad (4.40)$$

For a Coulomb potential, S_3 reduces to

$$(S_3)_{Coul} = -6c^2 E_0 + 4c^2 \langle \psi_0 | V_{Coul} | \psi_0 \rangle. \quad (4.27)$$

In the next chapter we will use these results to test the completeness requirements of the variational basis set.

CHAPTER V
TESTS OF THE BASIS SET

Results for the Relativistic Sum Rules

In order to test the assumption (4.3) for the basis set, i.e.,

$$(H - \omega)^k - \sum_{j=1}^N |\psi_j^{\text{var}}\rangle \langle \psi_j^{\text{var}}| (E_j^{\text{var}} - \omega)^k = \epsilon \quad (5.1a)$$

with

$$\epsilon \xrightarrow[N \rightarrow \infty]{} 0, \quad (5.1b)$$

we will specialize the results obtained in the last section for the relativistic sum rules, to the case in which ψ_0 is the wavefunction for the ground state ($1s_{1/2}$) of a one-electron atom. Then, we will perform explicitly the sums in the sum rules, we will compare the results with the exact ones, and under a variation of the dimension of the basis set we shall check assumption (5.1b).

The wave function for an electron in a $s_{1/2}$ state is given in A.U. by¹⁵

$$g = \left[\frac{(1+\gamma)}{2\pi(2\gamma+1)} 2\lambda \right]^{\frac{1}{2}} (2\lambda r)^{\gamma} e^{-\lambda r} \quad (5.2a)$$

and

$$f = - \left[\frac{1-\gamma}{1+\gamma} \right]^{\frac{1}{2}} g. \quad (5.2b)$$

We shall use the integral

$$A = \int_0^\infty e^{-ar} r^b dr \quad (5.3a)$$

with a and b being real numbers satisfying the conditions $a > 0$ and $b > -1$.

The result for A is¹⁶

$$A = \frac{1}{a^{(b+1)}} \Gamma(b+1) \quad (5.3b)$$

With the aid of A we find

$$I_n = \int_{\gamma_0}^{\gamma} r^n \psi(r)^2 dr =$$

$$= \frac{(2\lambda)^{2\gamma}}{\Gamma(2\gamma+1)} \int_0^\infty e^{-2\lambda r} r^{2\gamma+n} dr =$$

$$= (2\lambda)^{-n} \frac{\Gamma(2\gamma+n+1)}{\Gamma(2\gamma+1)} \quad (5.4)$$

where the value of 2γ lies between $2\gamma=1.9999$ for $Z=1$ and $2\gamma=1.0169$ for $Z=118$. As a consequence, the highest value of Z that will satisfy the conditions for the use of (5.3) in the case I_{-2} is $Z=118$.

We note that I_0 yields the normalization condition $I_0=1$.

Using for the ground state

$$\lambda = \bar{x}, \quad \gamma = \sqrt{1 - (\alpha \bar{x})^2} \quad \text{and} \quad E_0 = \frac{\gamma}{\alpha^2},$$

we obtain

$$I_n = (2z)^{-n} \frac{\Gamma(2\gamma+n+1)}{\Gamma(2\gamma+1)} \quad (5.5)$$

and then,

$$S_0 = I_2 = \frac{1}{2z^2} (\gamma+1)(2\gamma+1) \quad (5.6)$$

and

$$\begin{aligned} S_3 &= -\frac{6}{\alpha^2} E_0 - \frac{4z}{\alpha^2} I_{-1} = -\frac{1}{\alpha^2} \left(6E_0 + \frac{4z^2}{\gamma} \right) = \\ &= -\frac{1}{\alpha^4} 6\gamma + \frac{4(1-\gamma^2)}{\gamma} \end{aligned}$$

Finally,

$$S_3 = -\frac{2}{\alpha^4} \left(\gamma + \frac{2}{\gamma} \right) \quad (5.7)$$

To obtain S_4 , we first derive an expression for

$$\nabla^2 [h(r) Y_{lm}(\theta, \varphi)] = (\nabla^2 h) Y_{lm} + 2(\nabla h) \cdot (\nabla Y_{lm}) + h \nabla^2 Y_{lm}.$$

Using

$$(\nabla h(r)) \cdot (\nabla Y_{lm}(\theta, \varphi)) = 0$$

and

$$\frac{L^2}{r^2} Y_{lm} = -\nabla^2 Y_{lm} = \frac{\ell(\ell+1)}{r^2} Y_{lm},$$

we obtain

$$\nabla^2 \left[h(r) Y_{\ell m}(\theta, \varphi) \right] = (\nabla^2 h) Y_{\ell m} - \frac{h}{r^2} \ell(\ell+1) Y_{\ell m} . \quad (5.8)$$

In our case

$$\nabla^2 \psi = \begin{pmatrix} i \nabla^2 \left(\frac{q}{r} \right) \Omega_{jLM} \\ -\nabla^2 \left(\frac{f}{r} \right) \Omega_{jLM} \end{pmatrix} - \begin{pmatrix} i \ell(\ell+1) \frac{q}{r^3} \Omega_{jLM} \\ -\ell(\ell+1) \frac{f}{r^3} \Omega_{jLM} \end{pmatrix} , \quad (5.9)$$

then, for the ground state:

$$\langle \psi_0 | \nabla^2 | \psi_0 \rangle = \int q \nabla^2 \left(\frac{q}{r} \right) r dr + \int f \nabla^2 \left(\frac{f}{r} \right) r dr - 2 \int \frac{f^2}{r^2} dr . \quad (5.10)$$

But

$$\nabla^2 \left[\frac{h(r)}{r} \right] = \frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \left(\frac{h}{r} \right) \right] = \frac{1}{r^2} \frac{d}{dr} \left(r \frac{dh}{dr} - h \right) = \frac{1}{r} \frac{d^2 h}{dr^2} \quad (5.11)$$

and in the case

$$h(r) = e^{-ar} r^b$$

we use

$$h' = \left(-a + \frac{b}{r} \right) h$$

to obtain

$$\frac{h''}{r} = \left[-\frac{b}{r^2} + \left(a - \frac{b}{r} \right)^2 \right] \frac{h}{r} .$$

In our case, for h denoting either g or f , (5.11) becomes

$$\nabla^2 \left(\frac{h}{r} \right) = \left[\vec{z}^2 - \frac{2\gamma z}{r} + \frac{\gamma(\gamma-1)}{r^2} \right] \frac{h}{r} \quad . \quad (5.12)$$

Using now (5.4) in (5.10):

$$\langle \psi_0 | \nabla^2 | \psi_0 \rangle = \vec{z}^2 - 2\gamma z I_{-1} + \gamma(\gamma-1) I_{-2} + (\gamma-1) I_{-2} =$$

$$= \vec{z}^2 - 2\gamma z I_{-1} + (\gamma^2 - 1) I_{-2} , \quad (5.13)$$

where we used (5.2) in the form

$$f^2 = \frac{(1-\gamma)}{2} (f^2 + g^2) . \quad (5.14)$$

Then, using (5.5) we obtain for (5.13):

$$\langle \psi_0 | \nabla^2 | \psi_0 \rangle = -\vec{z}^2 \left[1 - \frac{2(\gamma^2 - 1)}{\gamma(2\gamma - 1)} \right] = \frac{\vec{z}^2(\gamma - 2)}{\gamma(2\gamma - 1)} . \quad (5.15)$$

Finally,

$$\begin{aligned} S_4 &= \frac{1}{\alpha^4} \left\{ -\frac{8\vec{z}^2(\gamma - 2)}{\gamma(2\gamma - 1)} + 12C^6 \right\} = \\ &= \frac{1}{\alpha^6} \left\{ \frac{8(\gamma^2 - 1)(\gamma - 2)}{\gamma(2\gamma - 1)} + 12 \right\} . \end{aligned} \quad (5.16)$$

We can now summarize the results obtained:

$$S_0 = \frac{1}{2\chi^2} (\gamma + 1)(2\gamma + 1), \quad (5.6)$$

$$S_1 = 0, \quad (4.13)$$

$$S_2 = \frac{3}{\alpha^2} \quad (4.16)$$

$$S_3 = -\frac{2}{\alpha^4} \left(\gamma + \frac{2}{\gamma} \right) \quad (5.7)$$

$$S_4 = \frac{4}{\alpha^6} \left\{ \frac{2(\gamma^2 - 1)(\gamma - 2)}{\gamma(2\gamma - 1)} + 3 \right\}. \quad (5.16)$$

Variational Calculation of the Sum Rules

We shall now calculate the sum rules by the direct evaluation of

$$S_k = \sum_j (E_j - E_0)^k |\langle \psi_j | F | \psi_0 \rangle|^2, \quad (5.17)$$

where the sum runs over all the variational eigenvectors with J-values allowed by the transition.

The matrix elements $\langle \psi_j | r_k | \psi_0 \rangle$ can be calculated directly in terms of the basis vectors

$$\hat{\psi}_{jLM}^{(P)} = \frac{i}{N(P,P)} \frac{\vec{r}^{(P)}}{r} \begin{pmatrix} \Omega_{jLM} \\ 0 \end{pmatrix}$$

$$\hat{\omega}_{j\ell M}^{(p)} = -\frac{1}{N(p,p)} \cdot \frac{\vec{z}^{(p)}}{r} \begin{pmatrix} 0 \\ \Omega_{j\ell M} \end{pmatrix} \quad (2.11)$$

with

$$\vec{z}^{(p)} = e^{-\lambda r} r^{\lambda+p}, \quad p=0, 1, 2, \dots, N$$

$$N(p,p) = \frac{\Gamma(2\lambda + p + p' + 1)}{\lambda^{(2\lambda + p + p' + 1)}}$$

After the diagonalization of the Hamiltonian, the eigenvectors can be expressed in terms of the basis vectors by linear combinations of the type

$$\psi_k = \sum_p \left\{ a_k^{(p)} \hat{\omega}_{j\ell M}^{(p)} + b_k^{(p)} \hat{\omega}_{j\ell M}^{(p)} \right\} \quad (5.18)$$

and then, noting that

$$\langle \hat{\omega} | \vec{F} | \hat{\omega} \rangle = 0, \quad (5.19)$$

we have

$$\begin{aligned} |\langle \psi_k^{j\ell M'} | \vec{F} | \psi_o^{j\ell M} \rangle|^2 &= \sum_{pp'} \left| \left\{ a_k^{(p')} a_o^{(p)} \langle \hat{\omega}_{j\ell M'}^{(p')} | \vec{F} | \hat{\omega}_{j\ell M}^{(p)} \rangle + \right. \right. \\ &\quad \left. \left. + b_k^{(p')} b_o^{(p)} \langle \hat{\omega}_{j\ell M'}^{(p')} | \vec{F} | \hat{\omega}_{j\ell M}^{(p)} \rangle \right\} \right|^2. \end{aligned} \quad (5.20)$$

As a direct consequence of definitions (2.11) we obtain:

$$\langle \hat{\psi}_{j\ell M}^{(p)} | \vec{r} | \hat{\psi}_{j\ell M}^{(p)} \rangle = \langle \hat{\psi}_{j\ell M}^{(p)} | \vec{r} | \hat{\psi}_{j\ell M}^{(p)} \rangle. \quad (5.21)$$

Then, calling

$$D_{q'qP'P}(j'j; \ell'_1 \ell_2 \ell'_3 \ell_4) = \frac{1}{3} \sum_k \langle \hat{\psi}_{j\ell_3 M}^{(q)} | x_k^+ | \hat{\psi}_{j'\ell'_2 M'}^{(q')} \rangle \langle \hat{\psi}_{j\ell_1 M}^{(p)} | x_k^- | \hat{\psi}_{j'\ell'_4 M'}^{(p)} \rangle \quad (5.22)$$

we can rewrite (5.20) as

$$\begin{aligned} \frac{1}{3} \sum_{M M'} & \left| \langle \psi_{k'}^{j\ell' M} | \vec{r} | \psi_{k'}^{j\ell M} \rangle \right|^2 = \sum_{\substack{PP' \\ q'q'}} \left\{ a_k^{(q)} a_o^{(q)} a_k^{(p)} a_o^{(p)} D_{q'qP'P}(j'j; \ell' \ell \ell' \ell) + \right. \\ & + b_k^{(q)} b_o^{(q)} b_k^{(p)} b_o^{(p)} D_{q'qP'P}(j'j; \tilde{\ell}' \tilde{\ell} \tilde{\ell}' \tilde{\ell}) + \\ & \left. + \left[a_k^{(q)} a_o^{(q)} b_k^{(p)} b_o^{(p)} + b_k^{(q)} b_o^{(q)} a_k^{(p)} a_o^{(p)} \right] D_{q'qP'P}(j'j; \tilde{\ell}' \tilde{\ell} \ell' \ell) \right\}, \end{aligned} \quad (5.23)$$

where we used

$$D_{q'qP'P}(j'j; \tilde{\ell}' \tilde{\ell} \ell' \ell) = D_{q'qP'P}(j'j; \ell' \ell \tilde{\ell}' \tilde{\ell}). \quad (5.24)$$

The last equality is obtained if we write (5.22) as a product of radial and angular contributions.

In (5.23) we summed over the final, and averaged over the initial degenerate magnetic substates.

We will calculate now $D_{q'qP'P}(j'j; l'_1 l_2 l'_3 l_4)$. Using (2.11) and

$$Y_k = r \sqrt{\frac{4\pi}{3}} Y_{1k}(\hat{r}) \quad (5.25)$$

in (5.22), we obtain

$$D_{q'q'p'p}(j'j; l'_1l_2l'_1l_1) = R_{K'K_2}^{q'q} R_{K_1K_1}^{p'p} \Theta(j'j; l'_1l_2l'_1l_1), \quad (5.26)$$

where

$$R_{K'K}^{q'q} = \int_0^\infty \frac{\tilde{f}_{K'}^{(q')} \tilde{f}_K^{(q)}}{N_{K'}(q', q) N_K(q, q)} r dr \quad (5.27)$$

and

$$\begin{aligned} \Theta(j'j; l'_1l_2l'_1l_1) &= \frac{4\pi}{9} \sum_{M'M}^k (-1)^k \langle \Omega_{j'l_2M} | Y_{1k} | \Omega_{j'l_1M'} \rangle \\ &\quad \cdot \langle \Omega_{j'l_1M'} | Y_{1k} | \Omega_{j'l_1M} \rangle. \end{aligned} \quad (5.28)$$

Using (1.15) we have:²¹

$$\Theta(j'j; l'_1l_2l'_1l_1) = \frac{4\pi}{9} \sum_{M'M}^k \sum_{\substack{m_1'm_2 \\ m_1'm_2 \\ \lambda_1 \lambda_2}} (-1)^k \langle \ell_2 m_2 \frac{1}{2} \mu_2 | j M \rangle \langle \ell_2' m_2' \frac{1}{2} \mu_2 | j' M' \rangle$$

$$\langle \ell_1' m_1' \frac{1}{2} \mu_1 | j' M' \rangle \langle \ell_1 m_1 \frac{1}{2} \mu_1 | j M \rangle$$

$$\langle Y_{\ell_2 m_2} | Y_{1-k} | Y_{\ell_2' m_2'} \rangle \langle Y_{\ell_1' m_1'} | Y_{1k} | Y_{\ell_1 m_1} \rangle =$$

$$= \frac{4\pi}{q} \sum_k \sum_{\substack{m_1 m_2 \\ M' M}} (-1)^k \langle \ell_2 m_2 \frac{1}{2} \mu_2 | j M \rangle \langle \ell_2' m_2' \frac{1}{2} \mu_2 | j' M' \rangle$$

$$\langle \ell_2' m_2' \frac{1}{2} \mu_2 | j' M' \rangle \langle \ell_2 m_2 \frac{1}{2} \mu_2 | j M \rangle \langle \ell_2' m_2' 1-k | \ell_2 m_2 \rangle$$

$$\langle \ell_1 m_1 1 k | \ell_1' m_1' \rangle \langle \ell_2 \| \gamma_1 \| \ell_2' \rangle \langle \ell_1' \| \gamma_1 \| \ell_1 \rangle =$$

$$= \frac{4\pi}{q} \langle \ell_2 \| \gamma_1 \| \ell_2' \rangle \langle \ell_1' \| \gamma_1 \| \ell_1 \rangle S. \quad (5.29)$$

Writing

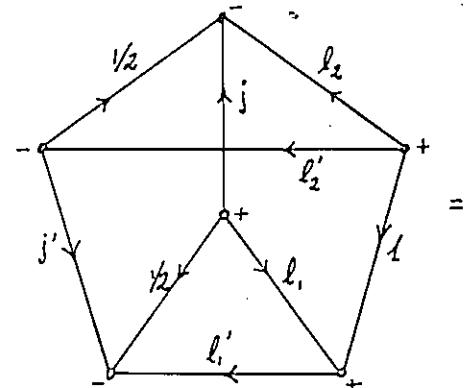
$$(-1)^k \langle \ell_2' m_2' 1-k | \ell_2 m_2 \rangle = (-1)^{\ell_2' - \ell_2} \frac{(2\ell_2 + 1)^{\frac{1}{2}}}{(2\ell_2' + 1)^{\frac{1}{2}}} \langle \ell_2 m_2 1 k | \ell_2' m_2' \rangle$$

and using the notation

$$[j_1, j_2] = (2j_1 + 1)(2j_2 + 1)$$

we can perform the sums in (5.29) graphically¹⁸ to obtain

$$S = [j, j'] [\ell_2, \ell_1']^{\frac{1}{2}} (-1)^{\ell_2' - \ell_2}$$



$$\begin{aligned}
 &= [j, j'] [\ell_2, \ell'_2]^{1/2} (-1)^{\ell_2 - \ell'_2} \\
 &\quad \begin{array}{c} \text{Diagram of a tetrahedron with vertices } j, j', i, i' \\ \text{edges labeled } \ell_2, \ell'_2, \ell_1, \ell'_1 \\ \text{and faces labeled } \frac{1}{2}, \frac{1}{2} \end{array} = \\
 &= [j, j'] [\ell_2, \ell'_2]^{1/2} (-1)^{\ell_2 + \ell'_2} \begin{Bmatrix} 1 & \ell_2 & \ell'_2 \\ \frac{1}{2} & j' & j \end{Bmatrix} \begin{Bmatrix} j' & \frac{1}{2} & \ell'_1 \\ \ell_1 & 1 & j \end{Bmatrix} = \\
 &= [j, j'] [\ell_2, \ell'_2]^{1/2} (-1)^{\ell'_1 + \ell_2} \begin{Bmatrix} 1 & \ell_2 & \ell'_2 \\ \frac{1}{2} & j' & j \end{Bmatrix} \begin{Bmatrix} 1 & \ell_1 & \ell'_1 \\ \frac{1}{2} & j' & j \end{Bmatrix}. \quad (5.30)
 \end{aligned}$$

Then, finally, using¹⁷

$$\langle \ell' || Y_1 || \ell \rangle = \left[\frac{3}{4\pi} (2\ell_1 + 1) \right]^{1/2} (-1)^{\ell_1 - \ell'} \begin{pmatrix} 1 & \ell' & \ell_1 \\ 0 & 0 & 0 \end{pmatrix} \quad (5.31)$$

we obtain

$$\begin{aligned}
 \theta(j, j', \ell'_1, \ell_2, \ell'_2, \ell_1) &= \frac{1}{3} [j, j'] [\ell_1, \ell'_1, \ell_2, \ell'_2]^{1/2} \begin{pmatrix} 1 & \ell_1 & \ell'_1 \\ 0 & 0 & 0 \end{pmatrix} \\
 &\quad \begin{pmatrix} 1 & \ell'_2 & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & \ell_2 & \ell'_2 \\ \frac{1}{2} & j' & j \end{Bmatrix} \begin{Bmatrix} 1 & \ell_1 & \ell'_1 \\ \frac{1}{2} & j' & j \end{Bmatrix}. \quad (5.32)
 \end{aligned}$$

In the case ψ_0 describes the ground state, we will have the following specializations of θ :

$$\theta(\frac{1}{2}, \frac{1}{2}, 1, 0, 1, 0) = 2/9$$

$$\theta(3/2 \frac{1}{2}, 1010) = 4/9 ,$$

$$\theta(3/2 \frac{1}{2}, 2121) = 4/9 .$$

For the radial contribution in (5.26) and for use in later calculations, it is convenient to define the generalized overlap integral

$$B^{2,1}_{(n_2, n_1)} = \frac{1}{N_2(n_2, n_2) N_1(n_1, n_1)} \int_0^\infty e^{-(\lambda_2 + \lambda_1)r} r^{\gamma_2 + \gamma_1 + n_2 + n_1} dr . \quad (5.33)$$

Using (5.3) we obtain

$$B^{2,1}_{(n_2, n_1)} = \frac{[(2\lambda_2)^{\gamma_2 + 2n_2 + 1} (2\lambda_1)^{\gamma_1 + 2n_1 + 1}]}{(\lambda_1 + \lambda_2)^{\gamma_1 + \gamma_2 + n_1 + n_2 + 1}}^{1/2}$$

$$\frac{\Gamma(\gamma_1 + \gamma_2 - 1)}{[\Gamma(2\gamma_1 - 1) \Gamma(2\gamma_2 - 1)]^{1/2}} \Phi(2, 1) , \quad (5.34a)$$

with

$$\Phi(2, 1) = \frac{(\gamma_1 + \gamma_2 + n_1 + n_2)}{[(2\gamma_1 + 2n_1)(2\gamma_2 + 2n_2)]^{1/2}} \cdot \frac{(\gamma_1 + \gamma_2 + n_1 + n_2 - 1)}{[(2\gamma_1 + 2n_1 + 2p - 2)(2\gamma_2 + 2n_2 + 2p - 3)]^{1/2}}$$

$$\frac{(\gamma_1 + \gamma_2 + 2n)}{[(2\gamma_1 + 2n)(2\gamma_2 + 2n)]^{1/2}} \cdot \frac{(\gamma_1 + \gamma_2 - 1)}{[(2\gamma_1 - 1)(2\gamma_2 - 1)]^{1/2}} \quad (5.34b)$$

where

$$n' = \max(n_1, n_2)$$

$$n = \min(n_1, n_2)$$

$$p = n' - n$$

$$\gamma' = \gamma_1 \text{ if } n_1 = n'$$

$$\gamma' = \gamma_2 \text{ if } n_2 = n'.$$

Formula (5.34b) describes the way in which $B^{2,1}(n_2, n_1)$ was calculated in order to avoid loss in numerical accuracy due to the large values of the gamma functions for high values of n_1 and n_2 .

Using (5.34), the radial contribution (5.27) becomes :

$$R_{K_1 K_2}^{P_2 P_1} = \frac{(\gamma_2 + \gamma_1 + P_2 + P_1 + 1)}{(\lambda_1 + \lambda_2)} B^{(2,1)}(P_2, P_1). \quad (5.35)$$

Numerical Evaluation of the Sum Rules

If assumption (5.1) were true, then for $N \rightarrow \infty$ we should obtain the exact values for the sum rules regardless of the exponential parameter used to generate \mathcal{A}_p . On the other hand, for finite values of N we would expect the error \mathcal{E} in (5.1) to be a function of the exponential parameter λ . If we define as plateau the continuous set of values of λ for which

$$\left| \frac{d\mathcal{E}}{d\lambda} \right| \approx 0, \quad \left| \frac{d^2\mathcal{E}}{d\lambda^2} \right| \approx 0 \quad (5.36)$$

then we would expect the interval of values of λ satisfying (5.36) to become larger as we increase the dimension N , with the limiting condition

$$\frac{d\mathcal{E}}{d\lambda} \xrightarrow[N \rightarrow \infty]{} 0 \quad \neq \lambda. \quad (5.37)$$

If we define by Δ_N the interval of values of λ for a given N for which (5.36) is satisfied, then the basis set must satisfy the following

two conditions:

$$\frac{\int_{\text{plateau}} \epsilon d\lambda}{\Delta_N} \xrightarrow[N \rightarrow \infty]{\longrightarrow} 0 \quad (5.38a)$$

and

$$\frac{1}{\Delta_N} \xrightarrow[N \rightarrow \infty]{\longrightarrow} 0. \quad (5.38b)$$

Conditions (5.38) imply (5.37), although conditions (5.37) and (5.38b) do not imply (5.38a). (i.e., the numerical sum could converge to the wrong value.)

As we see the selection of the plateau region can be quite arbitrary. This is the reason that both constraints (5.38) must be satisfied in order to show completeness of the basis set.

As a criterion to define a plateau, one could choose the region for which either one of the following criteria (or both) are satisfied

$$\left| \frac{d\epsilon}{d\lambda} \right| \leq A , \quad (5.39)$$

$$|\epsilon| \leq B \quad (5.40)$$

where ϵ can be either the absolute or the relative error.

If the exact value of the sum is not known, then the conditions

$$\frac{\int_{\text{plateau}} S_k d\lambda}{\Delta_N} \xrightarrow[N \rightarrow \infty]{\longrightarrow} \text{constant} , \quad (5.41a)$$

and

$$\frac{1}{\Delta_N} \xrightarrow[N \rightarrow \infty]{} 0 \quad (5.41b)$$

are necessary although not sufficient for completeness. In this case, \mathcal{E} must be substituted by S_k in (5.39) and (5.40).

As an example of the situations described by (5.38) and (5.41), Figure 5 displays a plot of the error in S_1 as a function of the exponential parameter λ and Figure 6 displays the positive energy contribution to S_1 as a function of λ . At first inspection we can see from the graphs that conditions (5.38) in the first case, and conditions (5.41) in the second, are satisfied. A more rigorous way to check if conditions (5.38) or (5.41) are satisfied by the basis set, is to fit to the data curves of the type

$$\bar{\mathcal{E}}_N = \left(\frac{1}{N}\right)^a f\left(\frac{1}{N}\right) \quad a > 0, f(0) = \text{constant} \neq 0 \quad (5.42a)$$

and

$$\frac{1}{\Delta_N} = \left(\frac{1}{N}\right)^b h\left(\frac{1}{N}\right) \quad b > 0, h(0) = \text{constant} \neq 0 \quad (5.42b)$$

Once the fitted curves are found, one can calculate the correlation coefficients between those curves and the actual data, and then, the levels of confidence for the rejection of the hypothesis of zero correlation.

For each sum rule, the dependence $\bar{\mathcal{E}}(\lambda)$ was numerically calculated for the case $Z = 50$, for values of λ ranging from 10 to 160 in jumps of $\delta\lambda = 10$. The plateau was defined as the region for which

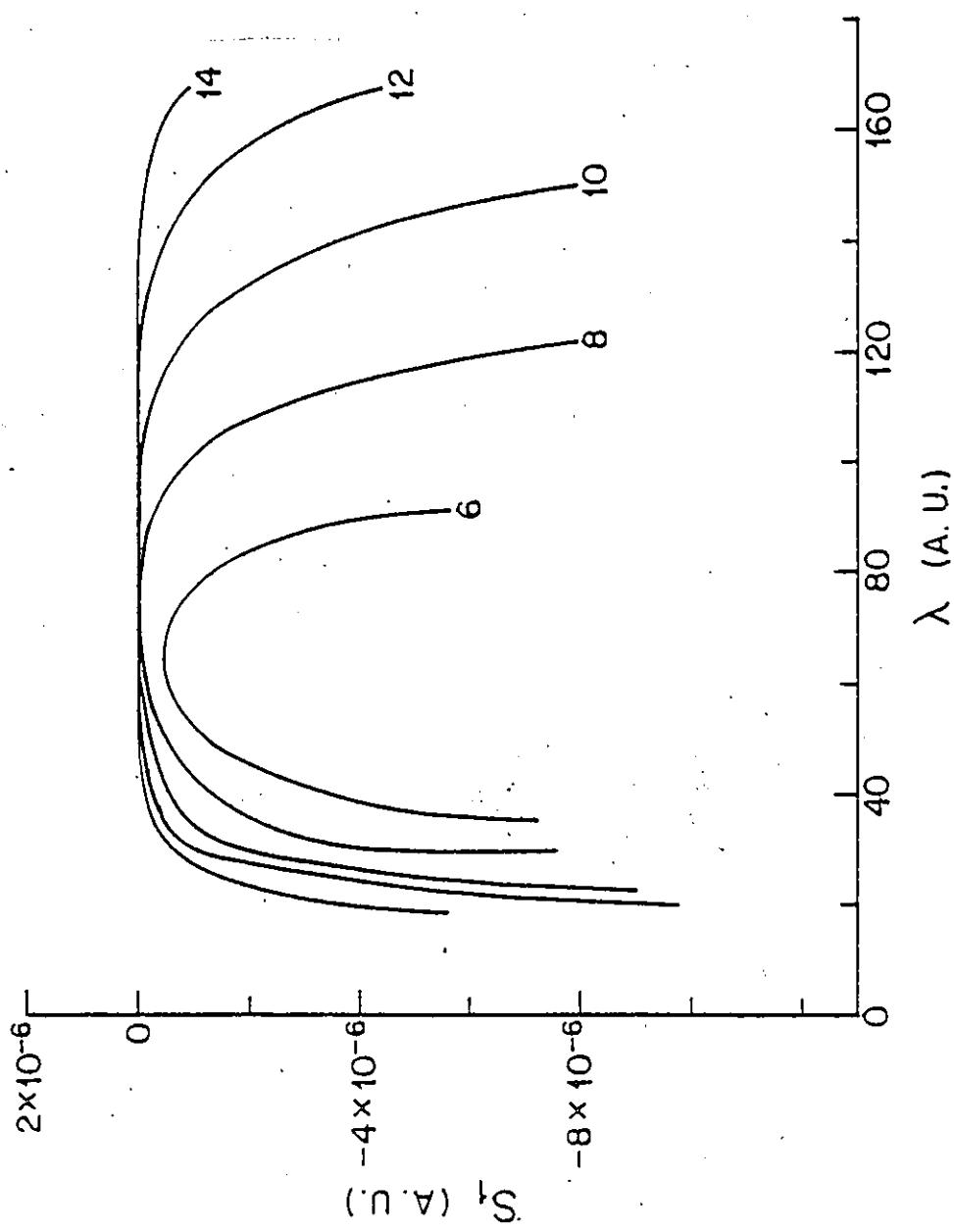


FIGURE 5. S_1 as a function of the exponential parameter λ for $Z=50$. The parameters on the curves show the dimension of the basis set.

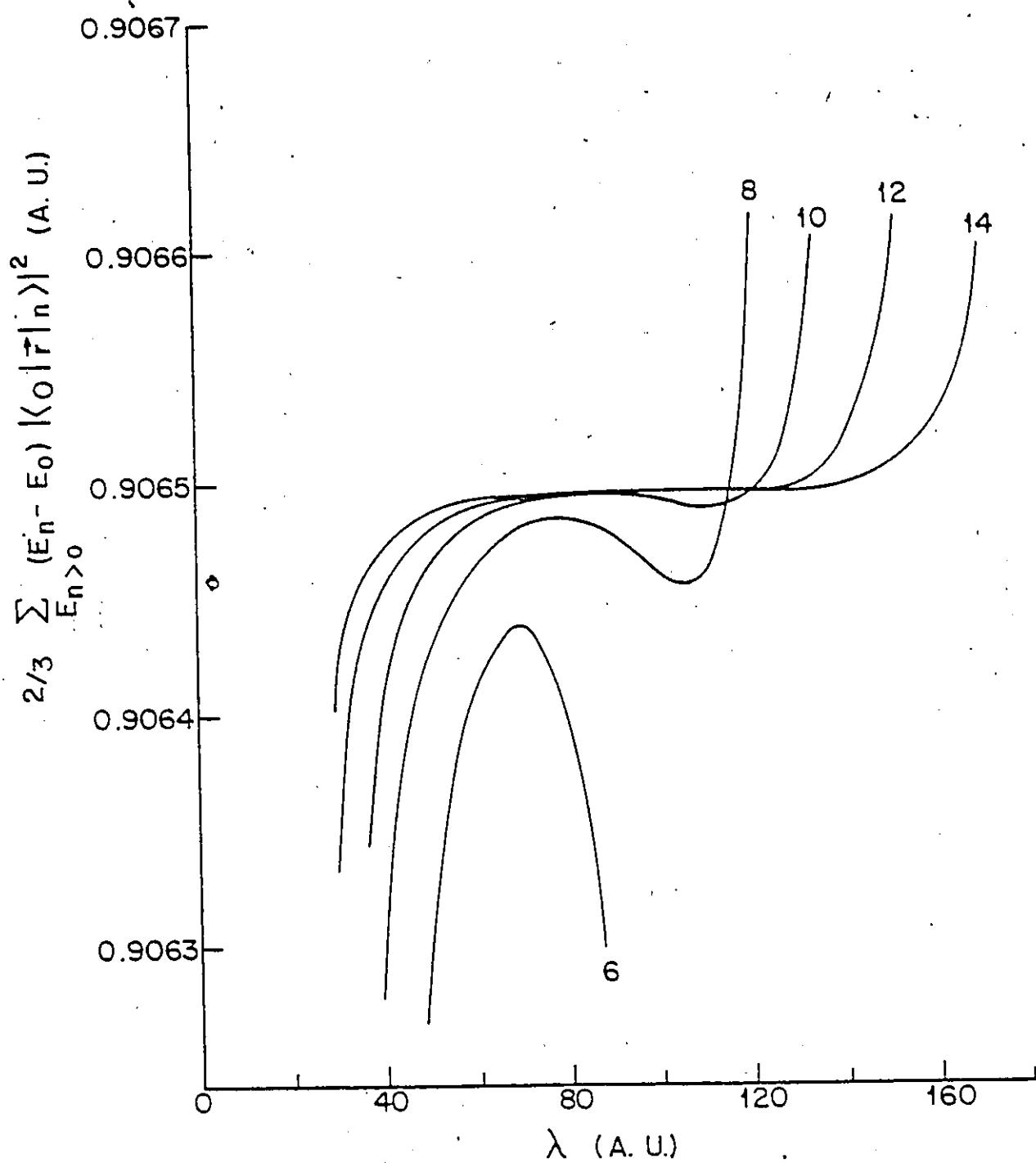


FIGURE 6. Positive energy contribution to S_1 as a function of the exponential parameter λ for $Z=50$. The parameters on the curves show the dimension of the basis set.

$$\frac{dS_i(\lambda)/d\lambda}{S_{iexact}} \leq \text{cutoff} \quad (5.43a)$$

except for S_1 for which

$$\frac{dS_1(\lambda)}{d\lambda} \leq \text{cutoff} \quad (5.43b)$$

was used.

The average error in the plateau was calculated as

$$\bar{\epsilon} = \left[\frac{1}{N} \sum_i \epsilon_i^2 + \frac{1}{2} (\epsilon_m^2 + \epsilon_M^2) \right]^{1/2}$$

where the sum runs over the n points inside the plateau and ϵ_m and ϵ_M are the extreme interpolated values for $\delta\lambda = 5$ in the regions where condition (5.43) is first (last) satisfied. This region is then defined as the complete plateau Δ_N .

The following results were obtained for basis sets with $N = 7, 8, 10, 12$ and 14 . To simplify the notation we will use: $x=1/N$, L.C.= level of confidence and C= cutoff.

For S_0 :

$$\bar{\epsilon} = x^5 / (44.3487 - 214.5728 x), \quad C=10^{-7}, \quad \text{L.C.}=100\%;$$

$$\Delta^{-1} = x^4 / (-4.418285 (-3) + 8.73231 x), \quad \text{L.C.}=99.1\%.$$

For S_1 :

$$\bar{\epsilon} = x^{1.5} / (5.56043 (5) - 2.85533 (6) x), \quad C=2 (-8), \quad \text{L.C.}=99.99\%;$$

$$\Delta^{-1} = x^5 / (-7.59749 (-4) + 1.34951 (-2) x), \text{L.C.}=99.97\%.$$

For S_2 :

$$\bar{\epsilon} = x^2 / (482.654 - 1978.67 x), C = 3 (-6), \text{L.C.}=99.97\%;$$

$$\Delta^{-1} = x / (7.94748 - 341.456 x^2), \text{L.C.}=99.65\%.$$

For S_3 :

$$\bar{\epsilon} = x^{1.5} / (692.557 - 2.26111 (4) x^2), C = 5 (-6), \text{L.C.}=99.999\%;$$

$$\Delta^{-1} = x (0.177528 - 3.95261 x^2), \text{L.C.}=99.2\%.$$

For S_4 :

$$\bar{\epsilon} = x (2.32515 (-2) + 0.172006 x^2), C = 4 (-5), \text{L.C.}=99.75\%;$$

$$\Delta^{-1} = x^{1/2} / (29.3632 - 1419.65 x^2), \text{L.C.}=99.99\%.$$

A number between parenthesis following a numeric constant denotes powers of ten.

The last results strongly suggest the completeness of the basis set. That is, that the basis set can provide a complete discrete representation of the Dirac-Green's function.

An interesting feature of the basis set is the Z-dependence of the error and the plateau size in the sums. For each sum, this dependence is shown in Figures 7 to 11. We note that both the plateau and the error tend to be larger for higher values of Z, although the behaviour of $\epsilon(\lambda)$ tends to be independent of Z outside the plateau region. That is, although

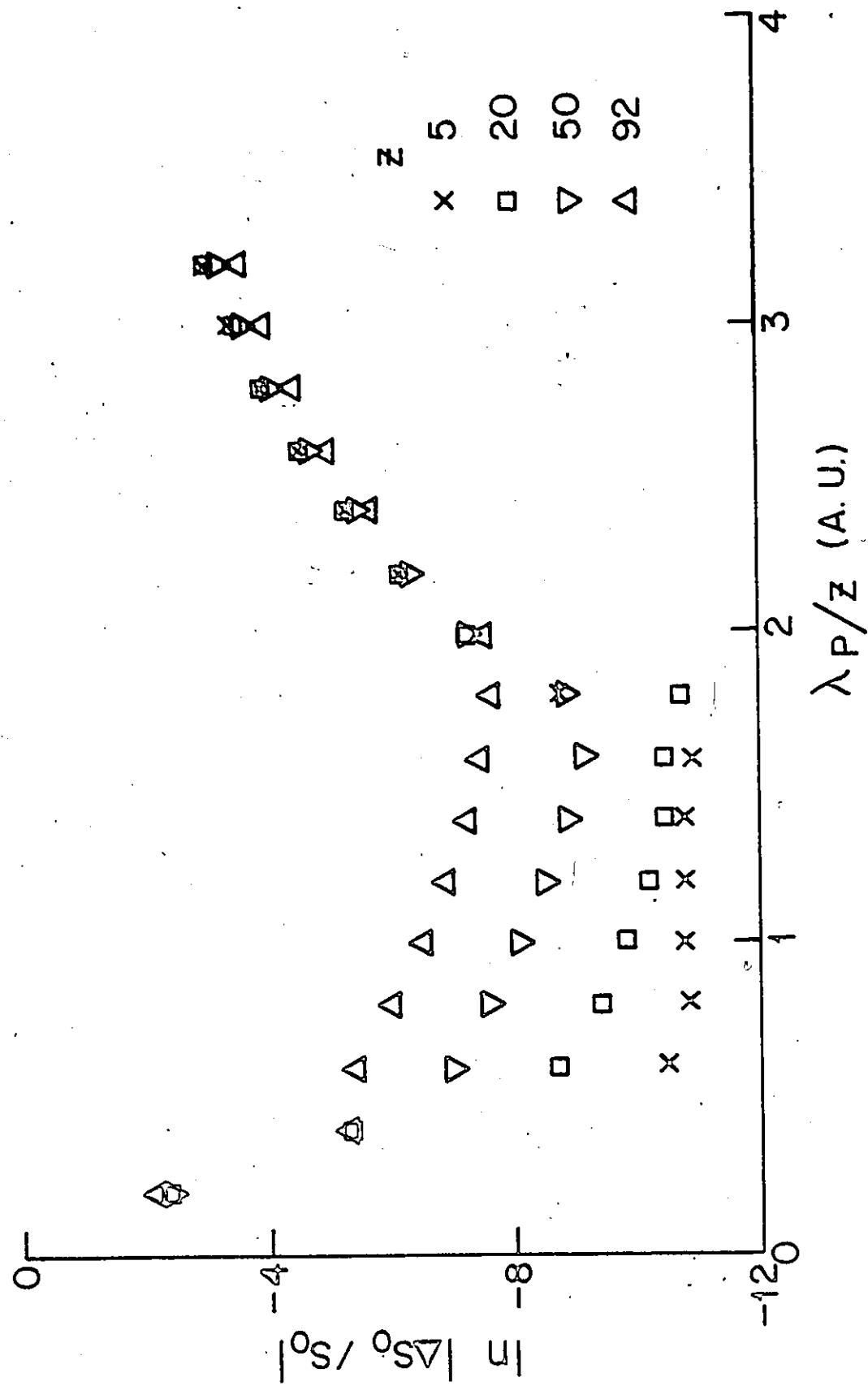


FIGURE 7. Z-dependence of the relative error in S_0 . λ_p is the exponential parameter used to generate the intermediate p-states.

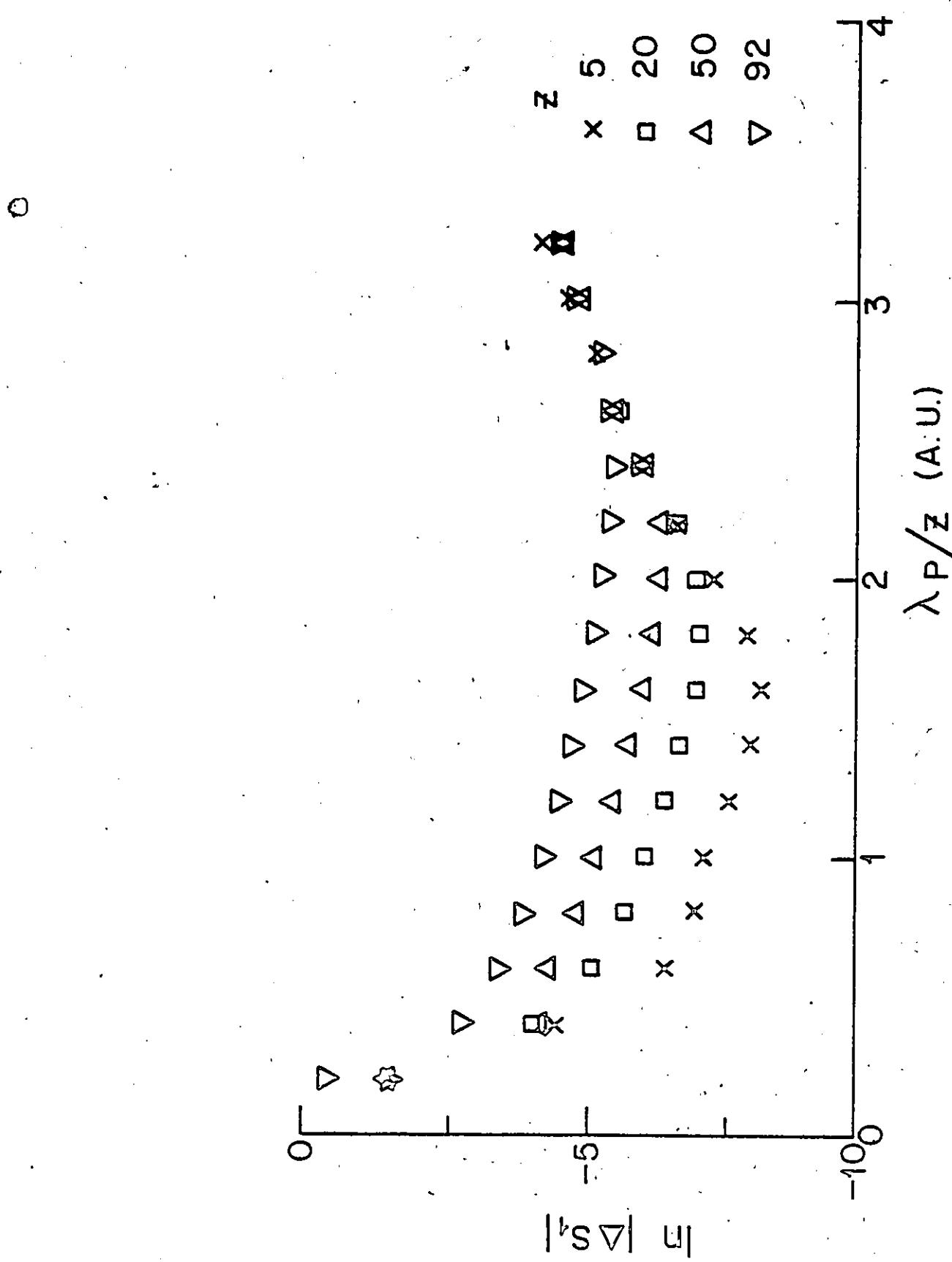


FIGURE 8. z -dependence of the error in S1. λ_p is the exponential parameter used to generate the intermediate p states.

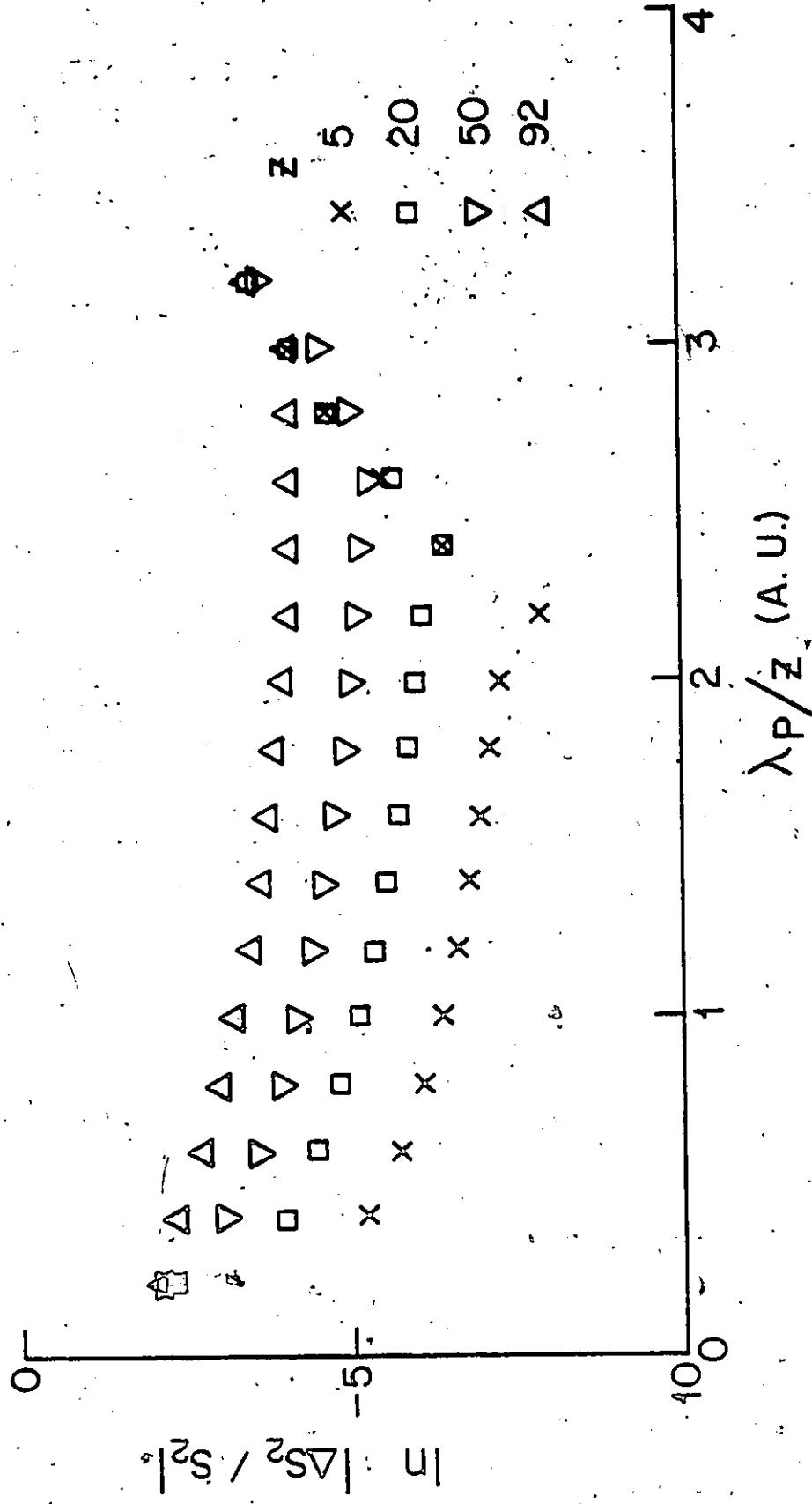


FIGURE 9. Z-dependence of the relative error in S_2 . λ_p is the exponential parameter used to generate the intermediate p states.

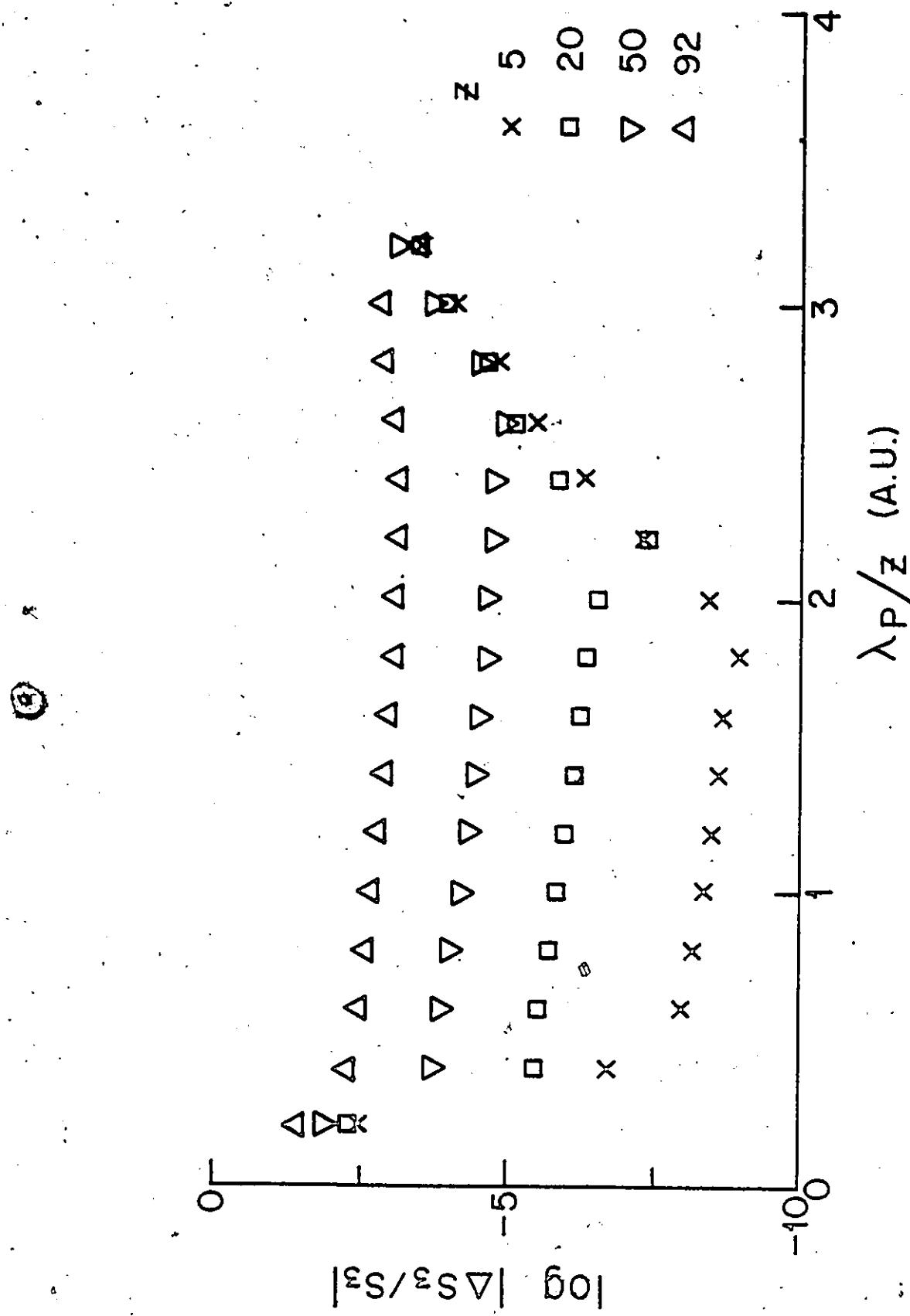


FIGURE 10. z -dependence of the relative error in S_3 . λ_p is the exponential parameter used to generate the intermediate p states.

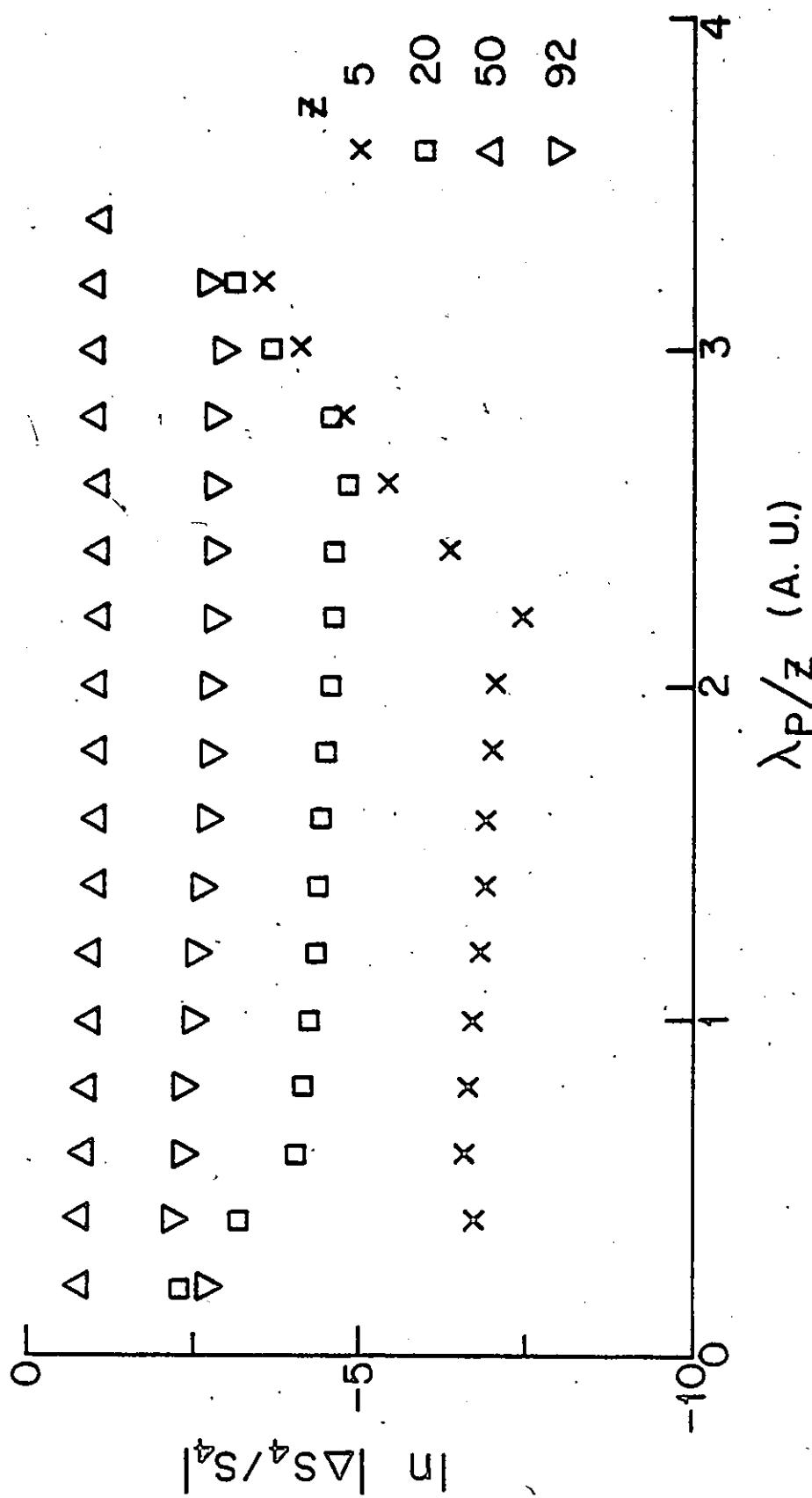


FIGURE 11. Z-dependence of the relative error in S_4 . λ_p is the exponential parameter used to generate the intermediate p states.

the stability is better for higher Z, the convergence is slower. A reason for this behaviour is the energy region covered by the variational eigenvalues. In units of the ionization energy, the maximum value for $E_{>0} - mc^2$ for $s_{1/2}$ states is 75.81 for Z=1 and 13.3 for Z=92. For $E_{<0} + mc^2$ the maximum values in units of the ionization energy are 105.3 for Z=1 and 51.2 for Z=92. We see that the variational representation of the high energy continuum gets poorer for higher Z. This gives rise to a larger error in the sum rules as the value of Z is increased. For the same reason, this difference in errors between low and high Z will become larger the higher the order of the sum rule becomes. This happens because the contribution of the high energy states becomes more important as the order of the sum rule is increased.

As a final remark in this section, we note that it is very simple in a finite basis set to obtain specific contributions to the total sum. In particular, we list in Tables 8 to 12 the contribution of the intermediate $p_{1/2}$ and $p_{3/2}$ levels for positive and negative energy states in each of the sum rules.

In conclusion, the results of this section provide strong evidence that the variational representation tends to a complete description of the exact set of solutions to the Dirac equation for an electron in the presence of a Coulomb potential, as the dimension of the basis set is enlarged.

The Contribution of the Positive Energy States

The exact sums S_i are functionally dependent only on Z, i.e., $S_i = S_i(Z)$. In the non-relativistic case, this dependence is obtained noticing that

TABLE 8
Contributions of Positive and Negative $p_{1/2}$ and $p_{3/2}$ Intermediate States to $(z^2/3)S_0$

z	POSITIVE $p_{1/2}$	POSITIVE $p_{3/2}$	POSITIVE TOTAL	NEGATIVE $p_{1/2}$	NEGATIVE $p_{3/2}$	NEGATIVE TOTAL	TOTAL	EXACT
1	0.333310	0.666646	0.999956	1.33119(-5)	1.62024(-14)	1.33119(-5)	0.999969	0.999969
5	0.332742	0.666149	0.998891	3.32233(-4)	1.35106(-10)	3.32233(-4)	0.999223	0.999223
10	0.330975	0.664595	0.995570	1.32199(-3)	7.94877(-9)	1.32200(-3)	0.996892	0.996892
20	0.324000	0.658364	0.982363	5.18219(-3)	4.11003(-7)	5.18260(-3)	0.987546	0.987546
50	0.278505	0.614047	0.892552	2.85466(-2)	5.55119(-5)	2.86021(-2)	0.921154	0.921154
92	0.170560	0.479091	0.649651	6.95493(-2)	1.12719(-3)	7.06764(-2)	0.720328	0.720328

TABLE 9
Contributions of Positive and Negative $P_{3/2}$ and $P_{1/2}$ Intermediate States to $(2/3)s_1$

Z	POSITIVE $P_{3/2}$	POSITIVE $P_{1/2}$	POSITIVE TOTAL	NEGATIVE $P_{3/2}$	NEGATIVE TOTAL	NEGATIVE $P_{1/2}$	TOTAL	EXACT
1	0.333301	0.666656	0.999955	-0.999956	-6.484(-10)	-0.999956	-6(-8)	0
5	0.332524	0.666371	0.998895	-0.998894	-4.22378(-8)	-0.998895	-7(-9)	0
10	0.330134	0.665488	0.995622	-0.995616	-6.12653(-6)	-0.995622	-9(-8)	0
20	0.321033	0.661991	0.983027	-0.982940	-8.30207(-5)	-0.983027	-8(-8)	0
50	0.268463	0.638035	0.906500	-0.9-4487	-2.00862(-3)	-0.906500	-4.7(-7)	0
92	0.163064	0.565806	0.729787	-0.715593	-1.41942(-2)	-0.729787	-3.3(-6)	0

TABLE 10
Contributions of Positive and Negative $p_{1/2}$ and $p_{3/2}$ Intermediate States to $(\alpha^2/3)S_2$

Z	POSITIVE $p_{1/2}$	POSITIVE $p_{3/2}$	POSITIVE TOTAL	NEGATIVE $p_{1/2}$	NEGATIVE TOTAL	NEGATIVE $p_{3/2}$	NEGATIVE TOTAL	TOTAL	EXACT
1	5.91479(-6)	1.18300(-5)	1.7748(-5)	0.999982	8.60187(-10)	0.999982	1.	1	1
5	1.46727(-4)	2.95444(-4)	4.42171(-4)	0.999557	4.42343(-7)	0.999558	1	1	1
10	5.74827(-4)	1.17818(-3)	1.75300(-3)	0.998240	6.64418(-6)	0.998247	1	1	1
20	2.15225(-3)	4.66768(-3)	6.81993(-3)	0.993089	9.06323(-5)	0.993179	0.999999	1	1
50	9.96805(-3)	2.81132(-2)	3.80812(-2)	0.959389	2.52348(-3)	0.961913	0.999994	1	1
92	1.90496(-2)	9.24833(-2)	1.11533(-1)	0.865868	2.25294(-2)	0.888398	0.9993	1	1

TABLE 11

Contributions of Positive and Negative $p_{1/2}$ and $p_{3/2}$ Intermediate States to $(\alpha^4/6)s_3$

Z	POSITIVE		POSITIVE		NEGATIVE		NEGATIVE		TOTAL		EXACT	
	$p_{1/2}$	$p_{3/2}$	TOTAL	$p_{1/2}$	TOTAL	$p_{3/2}$	TOTAL	$p_{1/2}$	TOTAL	$p_{3/2}$	TOTAL	
1	2.87370(-10)	5.44819(-10)	8.32189(-10)	-1.00001	-6.87515(-10)	-1.00001	-1.00001	-1.00001	-1.00001	-1.00001	-1.00001	
5	1.62430(-7)	3.34358(-7)	4.96788(-7)	-1.00022	-4.30976(-7)	-1.00022	-1.00022	-1.00022	-1.00022	-1.00022	-1.00022	
10	2.16385(-6)	5.19329(-6)	7.35714(-6)	-1.00089	-6.78227(-6)	-1.00090	-1.00089	-1.00089	-1.00089	-1.00089	-1.00089	
20	2.57634(-5)	7.38674(-5)	9.96308(-5)	-1.00365	-9.92094(-5)	-1.00375	-1.00365	-1.00365	-1.00365	-1.00365	-1.00365	
50	5.18196(-4)	2.26311(-3)	2.78131(-3)	-1.02575	-3.39799(-3)	-1.02915	-1.02637	-1.02638	-1.02637	-1.02638	-1.02638	
92	2.94388(-3)	2.38540(-2)	2.67978(-2)	-1.12932	-4.31888(-2)	-1.17251	-1.14571	-1.14657	-1.14571	-1.14657	-1.14657	

TABLE 12
 Contributions of Positive and Negative $p_{3/2}$ and $p_{1/2}$ Intermediate States to $(\alpha^6/12)S_4$

Z	POSITIVE $p_{1/2}$	POSITIVE $p_{3/2}$	POSITIVE TOTAL	NEGATIVE $p_{1/2}$	NEGATIVE $p_{3/2}$	NEGATIVE TOTAL	TOTAL	EXACT
1	1.71102(-13)	2.01425(-13)	3.72527(-13)	1.000002	6.87698(-10)	1.000002	1.000002	1.000002
5	1.81972(-9)	3.36479(-9)	5.18451(-9)	1.00088	4.42070(-7)	1.00088	1.00088	1.00088
10	4.18810(-8)	1.83222(-7)	2.25103(-7)	1.00356	7.08552(-6)	1.00357	1.00357	1.00357
20	1.14234(-6)	6.99780(-6)	8.14014(-6)	1.01466	1.13735(-4)	1.01478	1.01479	1.01481
50	1.15510(-4)	6.20863(-4)	7.36373(-4)	1.11056	5.16714(-3)	1.11573	1.11646	1.11818
92	1.91442(-3)	1.52721(-2)	1.71866(-2)	1.77209	1.16578(-1)	1.888866	1.90585	2.058

$$E_n \propto Z^2 \quad (5.44a)$$

and

$$\langle f | r | i \rangle \propto \frac{1}{Z} . \quad (5.44b)$$

Using (5.44), one obtains that the non-relativistic sum rules will be, for the ground state, of the form

$$S_i = a_i Z^{2(i-1)} \quad (5.45)$$

where the constants a_i are listed in (4.5):

In the relativistic case, the Z dependence of the positive energy states and the dipole matrix elements is more complicated than in (4.44). In this case, (4.45) can, in general, be written as

$$\frac{\vec{S}_i}{Z^{2(i-1)}} = b_i (\alpha z)^2 \quad (5.46)$$

with the functions b_i obeying the limiting condition

$$b_i \xrightarrow[\alpha z \rightarrow 0]{} a_i . \quad (5.47a)$$

The a_i 's are defined in (5.45), and S_i denotes the sum over positive energy states only.

We note that in the non-relativistic case, the sum S_4 diverges for the ground state. This implies



$$b_4 \xrightarrow[\alpha z \rightarrow 0]{} \infty \quad (5.47b)$$

In Table 13 we list the relativistic values of the sums over positive energy levels. To show that conditions (5.47) are satisfied, we obtained a functional approximation to $b_i((\alpha Z)^2)$ in (5.46), by interpolating the values of b_i at $Z = 1, 5, 10, 20$, and 92 .

The results obtained are:

$$(z^2/5)S_0^> = 1 - 0.850 (\alpha Z)^2 + 0.12 (\alpha Z)^4$$

$$(2/5)S_1^> = 1 - 0.82 (\alpha Z)^2 + 0.98 (\alpha Z)^4$$

$$(1/z^2)S_2^> = 1 - (\alpha Z)^2/(0.355 + 4.55(\alpha Z)^2 - 3.14 (\alpha Z)^4)$$

$$(1/(2z^4))S_3^> = 1 - (\alpha Z)^2/(0.011286 + 2.43(\alpha Z)^2)$$

$$(1/z^6)S_4^> = -10.2 - 11.15 \ln(\alpha Z)$$

A linear regression was made between the b_i 's and the interpolated values. For every sum the level of confidence for the rejection of the hypothesis of zero correlation was better than 99.9997%. This result strongly suggests that conditions (5.47) are satisfied.

TABLE 13
Positive Energy Contributions to the Sum Rules

	Z=1	Z=5	Z=10	Z=20	Z=50	Z=92	NON RELATIVISTIC
$(Z^2/3)S_0^>$	0.999956	0.998891	0.995570	0.982363	0.892552	0.649651	1.
$(2/3)S_1^>$	0.999955	0.998895	0.995622	0.983027	0.906500	0.729787	1
$(1/Z^2)S_2^>$	0.999696	0.996431	0.987595	0.960543	0.858159	0.742377	1
$(1/(2Z^4))S_3^>$	0.902	0.854	0.778	0.662	0.471	0.396	1
$(1/Z^6)S_4^>$	44.6	28.8	18.5	10.1	3.75	2.25	∞

CHAPTER VI

APPLICATIONS

Dipole Polarizability

The physical definition of polarizability arises when we consider an electron bound in an atom placed in a weak static external electric field.^{1,18}

Without loss of generality we assume the external field to be in the z-direction, i.e.,

$$\vec{E} = \epsilon \hat{z} \quad (6.1)$$

Let the atom be in a state $|\psi_0\rangle$ in the absence of the external field, and let $|\psi\rangle$ be the corresponding eigenvector in the presence of the external field. $|\psi\rangle$ will then satisfy the limiting condition:

$$|\psi\rangle \xrightarrow{\epsilon \rightarrow 0} |\psi_0\rangle \quad (6.2)$$

Applying bound state perturbation theory, we obtain to first order:

$$|\psi\rangle = |\psi_0\rangle + \epsilon \sum_n \frac{|n\rangle \langle n| z |\psi_0\rangle}{E_n - E_0}, \quad (6.3)$$

where the sum runs over a complete set of eigenvectors of the unperturbed Hamiltonian excluding $|\psi_0\rangle$. (We note that if $|\psi_0\rangle$ is a state of definite parity, then $\langle \psi_0 | z | \psi_0 \rangle = 0$.)

Using (6.3) we can calculate the perturbed dipole moment to first order:

$$\vec{P} = \langle \psi | \vec{F} | \psi \rangle =$$

$$= \vec{P}_0 + \epsilon \sum_n \left\{ \frac{\langle \psi_0 | \vec{z} | n \rangle \langle n | \vec{r} | \psi_0 \rangle}{E_n - E_0} + \frac{\langle \psi_0 | \vec{F} | n \rangle \langle n | \vec{z} | \psi_0 \rangle}{E_n - E_0} \right\} \quad (6.4)$$

$$= \vec{P}_0 + \epsilon \vec{\alpha} \quad (6.5)$$

The last term in (6.5) represents the induced dipole moment. $\vec{\alpha}$ is called the polarizability.

Only the z-component in \vec{r} contributes to (6.4), then,

$$\vec{\alpha} = \hat{z} \alpha \quad (6.6)$$

with

$$\alpha = 2 \sum_n \frac{|\langle \psi_0 | \vec{z} | n \rangle|^2}{E_n - E_0} \quad (6.7)$$

We obtained the relativistic values of the polarizability for the ground state of hydrogenic ions using

$$\alpha = \frac{2}{3} S_z = \frac{2}{3} \sum_n \frac{|K| \vec{F}|_{10}\rangle|^2}{E_n - E_0} \quad (6.8)$$

In Table 14 we list the results obtained for $Z^4 \alpha$, with the detailed contribution of the positive and negative $p_{1/2}$ and $p_{3/2}$ states. These results were obtained with a fourteen vector (twice). basis set.

TABLE 14
 Contributions of Positive and Negative $p_{1/2}$ and $p_{3/2}$ States
 to the Dipole Polarizabilities for Hydrogenic Ions

Z	POSITIVE		NEGATIVE		TOTAL		NEGATIVE		TOTAL	
	$p_{1/2}$	$p_{3/2}$	TOTAL	$p_{1/2}$	TOTAL	$p_{3/2}$	TOTAL	$p_{1/2}$	TOTAL	$p_{3/2}$
1	1.4998957	2.9998558	4.4997515	-7.0886(-10)	-4.9(-19)	-7.0886(-9)	-4.997515	-7.0886(-9)	-4.997515	-7.0886(-9)
2	1.4995829	2.9994231	4.4990060	-1.1338(-8)	-1.3(-16)	-1.1338(-8)	-1.3(-16)	-1.1338(-8)	-1.3(-16)	-1.1338(-8)
3	1.4990616	2.9987020	4.4977636	-5.7373(-8)	-3.2(-15)	-5.7373(-8)	-3.2(-15)	-5.7373(-8)	-3.2(-15)	-5.7373(-8)
4	1.4983320	2.9976925	4.4960245	-1.8120(-7)	-3.1(-14)	-1.8120(-7)	-3.1(-14)	-1.8120(-7)	-3.1(-14)	-1.8120(-7)
5	1.4973941	2.9963946	4.4937887	-4.4200(-7)	-1.8(-13)	-4.4200(-7)	-1.8(-13)	-4.4200(-7)	-1.8(-13)	-4.4200(-7)
6	1.4962483	2.9948083	4.4910566	-9.1557(-7)	-7.7(-13)	-9.1557(-7)	-7.7(-13)	-9.1557(-7)	-7.7(-13)	-9.1557(-7)
7	1.4948947	2.9929337	4.4878285	-1.6941(-6)	-2.6(-12)	-1.6941(-6)	-2.6(-12)	-1.6941(-6)	-2.6(-12)	-1.6941(-6)
8	1.4933338	2.9907709	4.4841046	-2.8859(-6)	-7.4(-12)	-2.8859(-6)	-7.4(-12)	-2.8859(-6)	-7.4(-12)	-2.8859(-6)
9	1.4915657	2.9883197	4.4798854	-4.6151(-6)	-1.9(-11)	-4.6151(-6)	-1.9(-11)	-4.6151(-6)	-1.9(-11)	-4.6151(-6)
10	1.4895909	2.9855804	4.4751714	-7.0216(-6)	-4.2(-11)	-7.0216(-6)	-4.2(-11)	-7.0216(-6)	-4.2(-11)	-7.0216(-6)
12	1.4850232	2.9792375	4.4642607	-1.44999(-5)	-1.7(-10)	-1.44999(-5)	-1.7(-10)	-1.44999(-5)	-1.7(-10)	-1.44999(-5)

Table 14 continued

Z	POSITIVE $p_{j/2}$	POSITIVE $p_{3/2}$	POSITIVE TOTAL	NEGATIVE $p_{j/2}$	NEGATIVE $p_{3/2}$	NEGATIVE TOTAL	TOTAL
14	1.4796344	2.9717427	4.4513771	-2.67335(-5)	-5.5(-10)	-2.67340(-5)	4.4513504
16	1.4734294	2.9630966	4.4365261	-4.53561(-5)	-1.5(-9)	-4.55538(-5)	4.4364807
18	1.4664136	2.9533001	4.4197137	-7.22065(-5)	-3.7(-9)	-7.22102(-5)	4.4196415
20	1.4585930	2.9423540	4.4009469	-1.093110(-4)	-8.2(-9)	-1.093192(-4)	4.4008376
22	1.4499743	2.9302592	4.3802335	-1.588651(-4)	-1.67(-8)	-1.588819(-4)	4.3800746
24	1.4405649	2.9170170	4.3575819	-2.232143(-4)	-3.19(-8)	-2.232463(-4)	4.3573586
26	1.4303728	2.9026284	4.3330011	-3.048340(-4)	-5.77(-8)	-3.048917(-4)	4.3326962
28	1.4194064	2.8870947	4.3065012	-4.063092(-4)	-9.95(-8)	-4.064087(-4)	4.3060948
30	1.4076751	2.8704175	4.2780925	-5.303141(-4)	-1.647(-7)	-5.304788(-4)	4.2775621
35	1.3750646	2.8237311	4.1987957	-9.570052(-4)	-5.034(-7)	-9.575086(-4)	4.1978382
40	1.3379009	2.7699334	4.1078342	-1.5855211(-3)	-1.3096(-6)	-1.5868307(-3)	4.1062474
45	1.2963699	2.7090548	4.0054247	-2.4594874(-3)	-3.0151(-6)	-2.4625025(-3)	4.0029622
50	1.2506757	2.6411303	3.8918060	-3.6204838(-3)	-6.3067(-6)	-3.6267905(-3)	3.8881792

Table 14 continued

Z	POSITIVE		POSITIVE		NEGATIVE		NEGATIVE		TOTAL	
	P _{1/2}	P _{3/2}	TOTAL	P _{1/2}	TOTAL	P _{3/2}	TOTAL	P _{3/2}	TOTAL	
55	1.2010396	2.5661985	3.7672381	-5.1061843(-3)	1.22125(-5)	-5.1183967(-3)	3.7621197			
60	-1.1476984	2.4843019	3.6320003	-6.9485620(-3)	-2.21978(-5)	-6.9707599(-3)	3.6250295			
65	1.0909039	2.3954861	3.4863900	-9.1721345(-3)	-3.82706(-5)	-9.2104051(-3)	3.4771796			
70	1.0309222	2.2997989	3.3307212	-1.1792209(-2)	-6.30945(-5)	-1.1855303(-2)	3.3188659			
75	0.9680328	2.1972892	3.1653220	-1.4813065(-2)	-1.001092(-4)	-1.4913174(-2)	3.1504088			
80	0.9025279	2.0880042	2.9905321	-1.8225994(-2)	-1.536557(-4)	-1.8379650(-2)	2.9721524			
85	0.8347123	1.9719860	2.8066983	-2.2007062(-2)	-2.291067(-4)	-2.2236169(-2)	2.7844621			
90	0.7649025	1.8492654	2.6141679	-2.6114395(-2)	-3.329995(-4)	-2.6447395(-2)	2.5877205			
95	0.6934256	1.7198523	2.4132779	-3.0484689(-2)	-4.731690(-4)	-3.0957858(-2)	2.3823200			
100	0.62061746	1.5837181	2.2043355	-3.5028393(-2)	-6.588760(-4)	-3.5687269(-2)	2.1686483			

In the non relativistic case, it can be shown that:¹⁸

$$\alpha_{\text{non-rel}} = 4.5 Z^{-4}. \quad (6.9)$$

Using the values listed in Table 14, we can find the relativistic correction to $\alpha_{\text{non-rel}}$ by polynomial interpolation. We obtained:

$$Z^4 \alpha = 4.5 - \frac{14}{3} (\alpha_{\text{fs}} Z)^2 + 0.55983 (\alpha_{\text{fs}} Z)^4, \quad (6.10)$$

where by α_{fs} we denote the fine structure constant. The error in the interpolated values ranges between 5(-9) for $Z=1$ and 6(-4) for $Z=100$.

Two - Photon Decay

In this section we present the results for the decay rates from the $2s_{1/2}$ metastable state in one electron atoms. We obtain a general expression which allows one to calculate the relativistic decay rates by means of the variational set, when each of the two photons can be of any electric or magnetic n-pole type. Calculations are then carried out for the case in which the transitions are of all combinations of E1, E2, M1, and M2 types.

Calculations of the two-E1 decay rate have been performed in the non-relativistic¹⁹ as well as in the relativistic case.⁷ A comparison between our results and the relativistic results obtained by Johnson⁷ is then presented.

Theory. The scattering matrix for the emission of two photons is given by⁸

$$S = 4\pi \int d^4x_1 \int d^4x_2 \left\{ \bar{\psi}_f(\vec{r}_1) \hat{A}_f S_c^{(e)}(x_1, x_2) \hat{A}_i \psi_i(\vec{r}_2) e^{i(t_1 E_f - t_2 E_i)} + \right. \\ \left. + \bar{\psi}_f(\vec{r}_1) \hat{A}_i S_c^{(e)}(x_1, x_2) \hat{A}_f \psi_i(\vec{r}_2) e^{i(t_1 E_f - t_2 E_i)} \right\} \quad (6.11)$$

where

$$S_c^{(e)}(x_1, x_2) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega e^{i\omega(t_1 - t_2)} \sum_n \frac{\gamma_n(\vec{r}_1) \bar{\psi}_n(\vec{r}_2)}{E_n + \omega} \quad (6.12)$$

is the electron propagator, and

$$\hat{A} = \gamma^\mu A_\mu = -i\beta \vec{\alpha} \cdot \vec{A} + i\beta A_0. \quad (6.13)$$

For photon states of definite momentum and polarization (plane waves) the vector potential is

$$\hat{A} = \frac{i\beta}{\sqrt{2\epsilon c}} \left[-\vec{\alpha} \cdot (\vec{e} + G \vec{k}) e^{i(\vec{k} \cdot \vec{r} - \omega t)} + G e^{i(\vec{k} \cdot \vec{r} - \omega t)} \right] \quad (6.14)$$

where \vec{e} is the polarization vector.

For photon states of definite angular momentum and parity (spherical waves), the vector potential is for electric L-pole transitions:

$$\hat{A}_{LM} = \frac{i}{4\pi} \sqrt{\frac{\epsilon}{c}} \beta \left[-\vec{\alpha} \cdot (\vec{\alpha}_{LM}^{(1)} + G \vec{\alpha}_{LM}^{(2)}) + G \Phi_{LM} \right] e^{-i\omega t} \quad (6.15)$$

and for magnetic L-pole transitions:

$$\hat{A}_{LM} = \frac{-i}{4\pi} \sqrt{\frac{\omega}{c}} \beta \vec{\alpha} \cdot \vec{\alpha}_{LM}^{(o)} e^{-i\omega t} \quad (6.16)$$

where

$$\vec{a}_{LM}^{(L)} = i^{(L+1)} \left\{ \left[\frac{L}{2L+1} \right]^{1/2} j_{L+1} \left(\frac{\omega}{c} r \right) \vec{Y}_{L,L+1,M} - \left[\frac{L+1}{2L+1} \right]^{1/2} j_{L-1} \left(\frac{\omega}{c} r \right) \vec{Y}_{L,L-1,M} \right\} \cdot 4\pi \quad (6.17a)$$

$$\vec{a}_{LM}^{(L)} = i^{(L-1)} \left\{ \left[\frac{L+1}{2L+1} \right]^{1/2} j_{L+1} \left(\frac{\omega}{c} r \right) \vec{Y}_{L,L+1,M} + \left[\frac{L}{2L+1} \right]^{1/2} j_{L-1} \left(\frac{\omega}{c} r \right) \vec{Y}_{L,L-1,M} \right\} \cdot 4\pi \quad (6.17b)$$

$$\vec{a}_{LM}^{(L)} = i^L j_L \left(\frac{\omega}{c} r \right) \vec{Y}_{L,L,M} \cdot 4\pi, \quad \Phi_{LM} = i^L j_L Y_{LM} \cdot 4\pi. \quad (6.17c)$$

In (6.17) the j_L are the spherical Bessel functions:¹

$$j_L(\rho) = \left(\frac{\pi}{2\rho} \right)^{1/2} J_{L+1/2}(\rho), \quad (6.18)$$

and the $\vec{Y}(\hat{n})$ are the vector spherical harmonics:¹⁷

$$\vec{Y}_{lm}(\hat{n}) = \sum_{m\mu} \langle lm | \mu | jM \rangle Y_{lm}(\theta) \hat{n}_\mu. \quad (6.19)$$

In (6.14) and (6.15) G is the gauge variable. It is shown in Appendix B that the results are independent of G , so without loss of generality we could proceed now using $G=0$. Later on, we shall check the gauge invariance of the results obtained with the variational basis set by adding a gauge dependent term to the transverse electric field.

Substituting (6.12) and (6.14) in (6.11), we obtain

$$S = \frac{-c^2}{i\sqrt{\omega_i\omega_f}} \sum_n \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} d\omega.$$

$$\left\{ \frac{\langle \psi_f | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | \psi_i \rangle}{E_n + \omega} e^{it_1(E_f + \omega_f + \omega) - it_2(E_i - \omega_i + \omega)} + \right. \\ \left. + \frac{\langle \psi_f | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | \psi_i \rangle}{E_n + \omega} e^{it_1(E_f + \omega_i + \omega) - it_2(E_i - \omega_f + \omega)} \right\} \quad (6.20)$$

where the sum includes integration over the positive and negative continua.

Using

$$\int_{-\infty}^{\infty} e^{it\omega} dt = 2\pi \delta(\omega) \quad (6.21)$$

we obtain

$$S = \frac{-4\pi^2 c^2}{i(\omega_i \omega_f)^{1/2}} \sum_n \int_{-\infty}^{\infty} d\omega \left\{ \frac{\langle f | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | i \rangle}{E_n + \omega} \delta(E_f + \omega_f + \omega) \delta(E_i - \omega_i + \omega) + \right. \\ \left. + \frac{\langle f | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | i \rangle}{E_n + \omega} \delta(E_f + \omega_i + \omega) \delta(E_i - \omega_f + \omega) \right\} = \\ = \frac{4\pi^2 i c^2}{(\omega_i \omega_f)^{1/2}} \sum_n \left\{ \frac{\langle f | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | i \rangle}{E_n - E_f + \omega_f} + \right. \\ \left. + \frac{\langle f | \vec{\alpha} \cdot \vec{e}_i e^{-i\vec{k}_i \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_f e^{-i\vec{k}_f \cdot \vec{r}} | i \rangle}{E_n - E_i + \omega_f} \right\} \delta(E_i - E_f - \omega_i - \omega_f) \quad (6.22)$$

Calling

$$S = -2\pi i U \delta(E_i - E_f - \omega_i - \omega_f), \quad (6.23)$$

the probability of emission of two photons with momenta \vec{k}_1 and \vec{k}_2 is given by

$$\int d\omega_{k_1 k_2} = 2\pi |U|^2 \delta(E_i - E_f - \omega_1 - \omega_2) \frac{d\vec{k}_1 d\vec{k}_2}{(2\pi)^6} \quad (6.24)$$

where

$$k = \frac{\omega}{c}$$

and

$$d\vec{k} = k^2 dk d\Omega_k.$$

Integrating (6.24) over $d\omega_2$ we obtain

$$\begin{aligned} \frac{d\omega_{\omega_1 \omega_2}}{d\omega_1} &= \frac{\omega_1 \omega_2}{8\pi^3 c^2} \left| \sum_n \left\{ \frac{\langle f | \vec{\alpha} \cdot \vec{e}_2 e^{i\vec{k}_2 \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_1 e^{-i\vec{k}_1 \cdot \vec{r}} | i \rangle}{E_n - E_i + \omega_1} + \right. \right. \\ &\quad \left. \left. + \frac{\langle f | \vec{\alpha} \cdot \vec{e}_1 e^{-i\vec{k}_1 \cdot \vec{r}} | n \rangle \langle n | \vec{\alpha} \cdot \vec{e}_2 e^{i\vec{k}_2 \cdot \vec{r}} | i \rangle}{E_n - E_i + \omega_2} \right\} \right|^2 d\Omega_k d\Omega_{k_2}. \quad (6.25) \end{aligned}$$

Using now a spherical wave expansion:⁸

$$\vec{e}^{(\lambda)} e^{-i\vec{k} \cdot \vec{r}} = \sum_{\lambda} \sum_{LM} \left[\vec{e}^{(\lambda)} \cdot \vec{Y}_{LM}^{(\lambda)}(\vec{k}) \right] \vec{a}_{LM}^{*(\lambda)}(k\vec{r}), \quad (6.26)$$

$$\bar{e}^{i\vec{k}\cdot\vec{r}} = \sum_{LM} Y_{LM}^{(k)} \phi_{LM}^*$$

where

$$\vec{Y}_{LM}^{(0)}(\vec{k}) = \vec{Y}_{L,L,M}^{(k)} = -i \vec{k} \times \nabla_{\vec{k}} Y_{LM}^{(k)} \quad (6.26a)$$

$$[L(L+1)]^{1/2}$$

$$\vec{Y}_{LM}^{(1)}(\vec{k}) = -i \vec{k} \times \vec{Y}_{LM}^{(0)}(\vec{k}) \quad (6.26b)$$

$$Y_{LM}^{(-1)}(\vec{k}) = \vec{k} \cdot Y_{LM}^{(0)}(\vec{k}) \quad (6.26c)$$

$$\int \vec{Y}_{LM}^{*(\lambda)} \cdot \vec{Y}_{LM'}^{(\lambda)} d\Omega = \delta_{LL'} \delta_{MM'} \delta_{\lambda\lambda'}, \quad (6.26d)$$

and the $e^{(j)}$ are independent polarization vectors satisfying

$$\vec{e}^{(j)*} \cdot \vec{e}^{(j')} = \delta_{jj'} ; \quad \vec{e}^{(3)} = \vec{k} .$$

Using the last relations, the time independent part of the operator \hat{A} in (6.14) has the partial wave expansion

$$\hat{A} = \beta \sum_{j,\lambda,L,M} \left[\vec{e}^{(j)} \cdot \vec{Y}_{LM}^{(\lambda)}(\vec{k}) \right] \tilde{\alpha}_{LM}^{*(\lambda)}(r) \frac{i}{\sqrt{2\omega_c}} \quad (6.27)$$

with

$$\tilde{\alpha}_{LM}^{(\lambda)} = \vec{\alpha} \cdot \vec{a}_{LM}^{(\lambda)} ; \quad \lambda = 0, 1 , \quad (6.28a)$$

$$\tilde{\alpha}_{LM}^{(t-1)} = G \left[\vec{\alpha} \cdot \vec{\alpha}_{LM}^{(t-1)} - \vec{F}_{LM} \right]. \quad (6.28b)$$

Replacing (6.27) in (6.25) and summing over polarizations, we obtain

$$\begin{aligned} \frac{d\omega_{\omega_1, \omega_2}}{d\omega_1} &= \frac{\omega_1 \omega_2}{8\pi^3 c^2} \sum_{L_1 L_2} \sum_{M_1 M_2} \sum_{\lambda_1 \lambda_2} \left\{ [\Theta'(2,1) + \Theta'(4,2)] [\Theta''(2,1) + \Theta''(4,2)] \right\} \\ &\quad \left[\sum_{S_1} (\vec{e}_1^{(S_1)} \cdot \vec{Y}_{L_1 M_1}^{(\lambda_1)}(\vec{k}_1)) (\vec{e}_1^{(S_1)*} \cdot \vec{Y}_{L_1' M_1'}^{(\lambda_1')}(\vec{k}_1))^* \right] d\Omega_{k_1} \\ &\quad \left[\sum_{S_2} (\vec{e}_2^{(S_2)} \cdot \vec{Y}_{L_2 M_2}^{(\lambda_2)}(\vec{k}_2)) (\vec{e}_2^{(S_2)*} \cdot \vec{Y}_{L_2' M_2'}^{(\lambda_2')}(\vec{k}_2))^* \right] d\Omega_{k_2} \end{aligned} \quad (6.29)$$

where

$$\Theta(b,c) = \sum_n \frac{\langle H | \tilde{\alpha}_{L_b M_b}^{*(\lambda)}(R_c F) | n \rangle \langle n | \tilde{\alpha}_{L_c M_c}^{*(\lambda)}(R_c F) | i \rangle}{E_i - E_b + \omega_c}. \quad (6.30)$$

Since the $\vec{e}^{(j)}$ form an orthonormal set of vectors, then for any two vectors \vec{A} and \vec{B} it follows that

$$\sum_s (\vec{e}^{(S)*} \cdot \vec{A}) (\vec{e}^{(S)} \cdot \vec{B}) = \vec{A} \cdot \vec{B}. \quad (6.31)$$

Using (6.26) and (6.31) we obtain

$$\begin{aligned} \int d\Omega_k \sum_s (\vec{e}^{(S)} \cdot \vec{Y}_{LM}^{(\lambda)}(\vec{k})) (\vec{e}^{(S)*} \cdot \vec{Y}_{L'M'}^{(\lambda')}(\vec{k}))^* &= \\ &= \int d\Omega_k \vec{Y}_{LM}^{(\lambda)}(\vec{k}) \cdot \vec{Y}_{LM}^{(\lambda)*} = \delta_{\lambda\lambda'} \delta_{LL'} \delta_{MM'} \end{aligned} \quad (6.32)$$

Integrating over angles in (6.29) and using (6.32) we obtain finally

$$\frac{d\omega}{d\omega_1} = \frac{\omega_1 \omega_2}{8\pi^3 C^2} \sum_{\substack{L_1 L_2 \\ M_1 M_2 \\ \lambda_1 \lambda_2}} \left| \Theta(2,1) + \Theta(1,2) \right|^2. \quad (6.33)$$

Using for the matrix elements appearing in Θ the notation and results obtained by Grant²⁰, and summing over final states and averaging over initial states, equation (6.33) becomes

$$\begin{aligned} \frac{d\omega}{d\omega_1} = & \frac{\omega_1 \omega_2}{(2\pi)^3 C^2} \frac{1}{(2j_i+1)} \sum_{\substack{L_1 L_2 \\ M_1 M_2 \\ \lambda_1 \lambda_2}} \sum_{n_r} \left| \sum_{n_i} \left\{ \frac{\langle f | \tilde{\alpha}_{L_1 M_1}^{(\lambda)} | n_r \rangle \langle n_r | \tilde{\alpha}_{L_2 M_2}^{(\lambda)*} | i \rangle}{E_{n_r} - E_i + \omega_1} \right. \right. \right. \\ & \left. \left. \left. + \frac{\langle f | \tilde{\alpha}_{L_2 M_2}^{(\lambda)*} | n_r \rangle \langle n_r | \tilde{\alpha}_{L_1 M_1}^{(\lambda)} | i \rangle}{E_{n_r} - E_i + \omega_2} \right\} \right|^2 \right| \quad (6.34) \end{aligned}$$

where $J = l + \frac{1}{2}$, and l is the orbital angular momentum quantum number of the intermediate states. By the subscripts i and f we denote the initial and final states respectively. The general matrix element is given by

$$\langle \alpha | \tilde{\alpha}_{L M}^{*(\lambda)} | \beta \rangle = (-1)^{2j_\alpha - m_\alpha - \frac{1}{2}} (i)^{L+1-\lambda} \left(\frac{4\pi}{2L+1} \right)^{\frac{1}{2}} [j_\alpha, j_\beta]^{\frac{1}{2}}$$

$$\begin{pmatrix} j_\alpha & L & j_\beta \\ -m_\alpha & M & m_\beta \end{pmatrix} \begin{pmatrix} j_\alpha & L & j_\beta \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \tilde{M}_{\alpha\beta}(L, \lambda, \omega) \quad (6.35)$$

where

$$\tilde{M}_{\alpha\beta}(L, 0, \omega) = \frac{2L+1}{[L(L+1)]^{\frac{1}{2}}} (K_\alpha + K_\beta) I_L^+(\omega) \quad (6.56a)$$

$$\tilde{M}_{\alpha\beta}(L, l, \omega) = \left[\frac{L}{L+1} \right]^{\nu_2} \left[(K_\alpha - K_\beta) I_{L+1}^+ + (L+1) I_{L+1}^- \right] - \\ - \left[\frac{L+1}{L} \right]^{\nu_2} \left[(K_\alpha - K_\beta) I_{L-1}^+ - L I_{L-1}^- \right] \quad (6.36b)$$

and

$$\tilde{M}_{\alpha\beta}(L, -l, \omega) = G \left[(2L+1) J^{(L)} + \right. \\ \left. + (K_\alpha - K_\beta) (I_{L+1}^+ + I_{L-1}^+) - L I_{L-1}^- + (L+1) I_{L+1}^- \right]. \quad (6.36c)$$

In (6.36c) G is the gauge variable, and the following notation was used:

$$I_L^\pm(\omega) = \int_0^\infty (g_\alpha f_\beta \mp f_\alpha g_\beta) j_L(\frac{\omega r}{c}) dr \quad (6.37a)$$

$$J^{(L)}(\omega) = \int_0^\infty (g_\alpha g_\beta + f_\alpha f_\beta) j_L(\frac{\omega r}{c}) dr \quad (6.37b)$$

with g and f denoting the radial parts of the large and small components respectively as defined in (1.14).

We introduce now the following notation

$$\Theta^J(b, a) = (2J+1)^{\nu_2} \sum_{m_J} \begin{pmatrix} j_f & L_b & J \\ -m_f & M_b & m_J \end{pmatrix} \begin{pmatrix} J & L_a & j_i \\ -m_J & M_a & m_i \end{pmatrix} (-1)^{m_J + m_f + 1} \quad (6.38)$$

$$\Delta^J(b, a) = \frac{[J, j_i, j_f]^{\nu_2}}{[L_a, L_b]^{\nu_2}} 4\pi \begin{pmatrix} J & L_b & j_f \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} J & L_a & j_i \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \quad (6.39)$$

$$\tilde{S}^J(b,a) = \Delta^J(b,a) \sum_{n_J} \frac{\tilde{M}_{fn}(L_b, \lambda_b, \omega_b) \tilde{M}_{ni}(L_a, \lambda_a, \omega_a)}{E_{\theta_J} - E_{n_i} + \omega_a}. \quad (6.40)$$

Using definitions (6.38), (6.39) and (6.40), we can rewrite (6.34) in the following way:

$$\frac{d\omega}{d\omega_a} = \frac{\omega_a \omega_b}{(2\pi)^3 c^2 (2j_i+1)} \sum_{\substack{L_a L_b \\ M_a M_b}} \sum_{\substack{\lambda_a \lambda_b \\ m_f m_i}} \left\{ \sum_J \left[\Theta^J(b,a) S^J(b,a) + \Theta^{J'}(a,b) S^J(a,b) \right] \right\}^2. \quad (6.41)$$

Using the sum rules,

$$\sum_{\substack{m_f m_i \\ M_a M_b}} \Theta^J(b,a) \Theta^{J'}(b,a) = \delta_{JJ'}, \quad (6.42a)$$

$$\sum_{\substack{m_f m_i \\ M_a M_b}} \Theta^J(b,a) \Theta^{J'}(a,b) = (-1)^{L_a + L_b + 2J'} [J, J']^{1/2} \begin{Bmatrix} j_i & L_a & J \\ j_f & L_b & J' \end{Bmatrix}, \quad (6.42b)$$

the final expression for the decay rate is

$$\begin{aligned} \frac{d\omega}{d\omega_a} = & \frac{\omega_a \omega_b}{(2\pi)^3 c^2 (2j_i+1)} \sum_{\substack{\lambda_a \lambda_b \\ L_a L_b}} \left\{ (S^J(b,a))^2 + (S^J(a,b))^2 + \right. \\ & \left. + 2 \sum_{J'} \left[(-1)^{L_a + L_b + 2J'} [J, J']^{1/2} \begin{Bmatrix} j_i & L_a & J \\ j_f & L_b & J' \end{Bmatrix} S^J(b,a) S^{J'}(a,b) \right] \right\}. \quad (6.43) \end{aligned}$$

Equation (6.43) gives the decay rate summed over polarizations for transitions from an initial state i to a final state f by the emission of two photons, expanded over photon states of definite angular momenta and parity.

The sums occurring in $S^J(a,b)$ can be performed explicitly, using the variational set of eigenvectors for the intermediate n_J states.

Results. Calculations were made for transitions between the $2s_{1/2}$ and $1s_{1/2}$ states.

Considering that

$$\frac{E_{2s_{1/2}} - E_{1s_{1/2}}}{c^2} \approx (\alpha z)^2 <_1$$

for the range $0 < z < 100$, the integrals (6.57) were calculated using¹⁶

$$\int_0^\infty e^{-\lambda r} r^{\gamma - \frac{1}{2}} J_{L+\frac{1}{2}}(\frac{\omega}{c}r) dr =$$

$$= \frac{(\frac{\omega}{zc\lambda})^{L+\frac{1}{2}} \Gamma(\gamma+L+1)}{\lambda^{\gamma+\frac{1}{2}} \Gamma(L+3/2)} F\left[\frac{\gamma+L+1}{2}, \frac{\gamma+L+2}{2}; \frac{L+3}{2}; -\left(\frac{\omega}{zc}\right)^2\right]. \quad (6.44)$$

With the notation introduced in (2.11), and calling

$$\gamma = \gamma_1 + \gamma_2 + p_1 + p_2$$

$$\lambda = \lambda_1 + \lambda_2$$

$$\beta_L(\gamma) = \frac{1}{\gamma} (\gamma+L)(\gamma+L-1)\dots(\gamma); \quad L \geq 0,$$

we obtain for the overlap integrals involving the spherical Bessel functions:

$$\int_{r_1}^{r_2} j_L(\gamma) dr = \frac{\sqrt{\pi}}{2^{L+1}} \left(\frac{\omega}{\lambda c}\right)^L \frac{B(2,1) \beta_L(\gamma)}{\Gamma(L+3/2)}$$

$$F\left[\frac{\gamma+L+1}{2}, \frac{\gamma+L+2}{2}; L+3/2; -\left(\frac{\omega}{\lambda c}\right)^2\right]. \quad (6.45)$$

We express the differential decay rate in the form⁷

$$\frac{dw}{dy} = \bar{x}^6 \left(\frac{9\alpha^6}{2^{10}}\right) \psi(y, \bar{x}) R_y, \quad (6.46)$$

where y is the fraction of the energy carried by one of the photons, i.e.,

$$y = \frac{\omega_a}{\omega_a + \omega_b}$$

In table 15, we list the results for $\psi(y, Z)$ for two-E1 transitions to intermediate p states, and for the combined decay to s,p and d intermediate states through electric dipole, electric quadrupole, magnetic dipole and magnetic quadrupole transitions. Tables 16 and 17 list in detail those contributions for the cases $Z=1$ and $Z=92$, and Figure 12 displays $\psi(y, Z)$ for $Z=1$ and $Z=92$. In Table 18 we list the detailed contribution to the integrated decay rates of the transitions to intermediate s,p, and d states, for a number of hydrogenic ions. Finally, Table 19 displays the total integrated decay rates and the contribution of two-E1 transitions, for a wide selection of values of Z .

The results obtained for two-E1 transitions disagree with those

TABLE 15

Frequency Distribution for Total and two-E1 Decay Rates
of the $2s_{\frac{1}{2}}$ Metastable State in Hydrogenic Ions

y	Z = 1		Z = 20		Z = 40	
	ψ_{2E1}^a	ψ_{total}	ψ_{2E1}	ψ_{total}	ψ_{2E1}	ψ_{total}
0.0625	2.05239	2.05239	1.94466	1.94467	1.71445	1.71463
0.1250	3.15792	3.15792	3.08514	3.08515	2.87780	2.87808
0.1875	3.84452	3.84452	3.78626	3.78628	3.61504	3.61538
0.2500	4.28435	4.28435	4.23829	4.23831	4.10049	4.10084
0.3125	4.56958	4.56958	4.53305	4.53308	4.42257	4.42273
0.3750	4.74855	4.74855	4.71882	4.71885	4.62785	4.62821
0.4375	4.84732	4.84732	4.82166	4.82168	4.74260	4.74297
0.5000	4.87892	4.87892	4.85461	4.85464	4.77954	4.77990

^a The function $\psi(y, Z)$ is defined in equation (6.46).

Table 15 continued

y	Z = 60		Z = 80		Z = 92	
	2E1	total	2E1	total	2E1	total
0.0625	1.41771	1.41842	1.12350	1.12509	0.963201	0.96367
0.1250	2.56639	2.56769	2.18844	2.19190	1.94249	1.94784
0.1875	3.34165	3.34325	2.97876	2.98340	2.72075	2.72839
0.2500	3.87229	3.87404	3.55198	3.55733	3.31064	3.31977
0.3125	4.23419	4.23602	3.95891	3.96468	3.74221	3.75229
0.3750	4.47001	4.47188	4.23158	4.23760	4.03739	4.04805
0.4375	4.60350	4.60539	4.38873	4.39488	4.20972	4.22070
0.500	4.64676	4.64866	4.44010	4.44629	4.26642	4.27750

TABLE 16
 Contribution of s, p and d Intermediate States
 to the Decay Rate of the $2S_{\frac{1}{2}}$ Metastable State for Z=1

y	$\psi(y, 1)$			TOTAL
	s and d states			
0.0625	1.781(-13)	1.179(-14)	4.669(-25)	1.899(-13)
0.1250	1.158(-12)	1.879(-13)	2.976(-24)	1.346(-12)
0.1875	3.130(-12)	7.597(-13)	7.005(-24)	3.890(-12)
0.2500	5.835(-12)	1.771(-12)	1.050(-23)	7.606(-12)
0.3125	8.778(-12)	3.045(-12)	1.209(-23)	1.182(-11)
0.3750	1.140(-11)	4.282(-12)	1.162(-23)	1.568(-11)
0.4375	1.319(-11)	5.175(-12)	1.049(-23)	1.837(-11)
0.5000	1.383(-11)	5.500(-12)	9.934(-24)	1.933(-11)

Table 16 continued

y	$\psi_{(J,1)}$			TOTAL
	2E1	E1M2	2M2	
p states				
0.0625	2.0323898	8.9433(-11)	2.2534(-23)	2.0323898
0.1250	3.1579157	1.2298(-10)	1.0189(-22)	3.1579157
0.1875	3.8445229	1.3322(-10)	1.9446(-22)	3.8445229
0.2500	4.2843459	1.3348(-10)	2.5803(-22)	4.2843459
0.3125	4.5695778	1.2991(-10)	2.7948(-22)	4.5695778
0.3750	4.7485496	1.2575(-10)	2.6992(-22)	4.7485496
0.4375	4.8473179	1.2270(-10)	2.5115(-22)	4.8473179
0.5000	4.8789164	1.2160(-10)	2.4240(-22)	4.8789164

TABLE 17
 Contribution of s, p and d Intermediate States
 to the Decay Rate of the $2S_{1/2}$ Metastable State for Z=92

y	2M1	2E2	E2M1	TOTAL
0.0625	1.609(-5)	5.554(-7)	6.428(-9)	1.665(-5)
0.1250	1.075(-4)	9.653(-6)	4.096(-8)	1.171(-4)
0.1875	2.972(-4)	4.159(-5)	1.006(-7)	3.389(-4)
0.2500	5.649(-4)	1.016(-4)	1.622(-7)	6.667(-4)
0.3125	8.631(-4)	1.809(-4)	2.052(-7)	1.044(-3)
0.3750	1.133(-3)	2.604(-4)	2.245(-7)	1.394(-3)
0.4375	1.320(-3)	3.190(-4)	2.279(-7)	1.640(-3)
0.5000	1.387(-3)	3.406(-4)	2.272(-7)	1.728(-3)

Table 17 continued

γ	(y, 92)			TOTAL
	p states	2E1	E1M2	
	2H2	Total		
0.0625	0.96320	2.0164(-3)	4.0365(-8)	0.96365
0.1250	1.04249	5.0235(-3)	3.0460(-7)	1.04772
0.1875	2.02075	7.0295(-3)	8.0557(-7)	2.02805
0.2500	3.031064	8.0458(-3)	1.0340(-6)	3.031910
0.3125	3.074221	9.030(-3)	1.0644(-6)	3.075125
0.3750	4.03739	9.0265(-3)	1.0755(-6)	4.04666
0.4375	4.020972	9.0338(-3)	1.0755(-6)	4.021906
0.5000	4.026642	9.0351(-3)	1.0742(-6)	4.027577
				4.027750

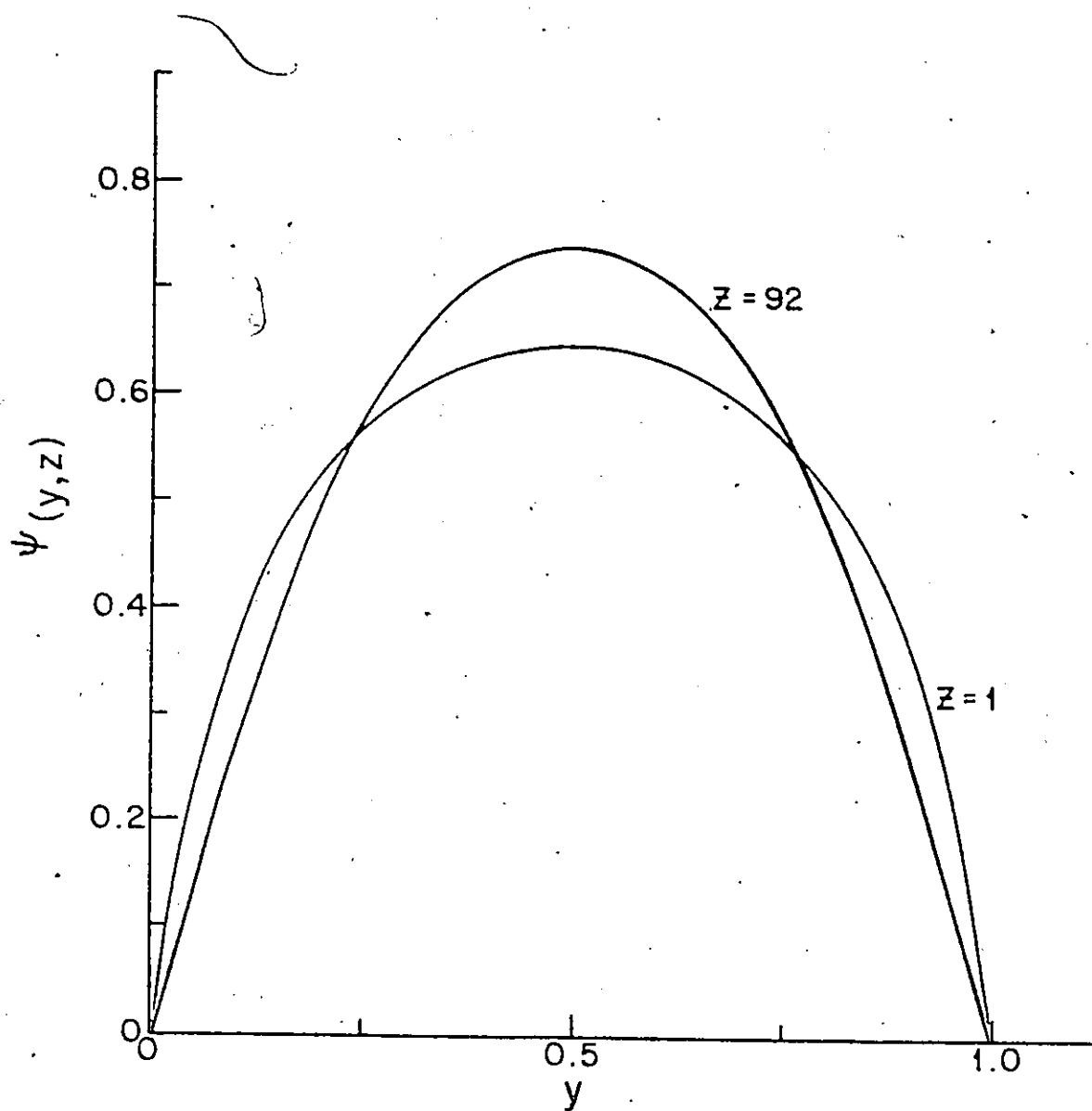


FIGURE 12. Frequency distribution of the differential decay rate for $Z=1$ and $Z=92$. The areas under the curves are normalized to one. The function $\psi(y, Z)$ is defined by equation (6.46).

TABLE 18
 Contribution of s, p and d Intermediate States
 to the Integrated Decay Rate of Hydrogenic Ions

Z	s and d States			TOTAL $10^{11} Z^{-10} w$
	2M1 (sec ⁻¹)	2E2 (sec ⁻¹)	E2M1 (sec ⁻¹)	
1	1.3804	4.9072	1.638	1.8711
20	1.4046	4.8739	1.732	1.8920
40	1.4778	4.7724	2.046	1.9551
60	1.6005	4.5974	2.721	2.0603
80	1.7737	4.3370	4.135	2.2076
92	1.9030	4.1290	5.752	2.3163

Table 18 continued

Z	p states				TOTAL $Z^{-6} w$ (sec $^{-1}$)
	2E1	E1M2	2D2	TOTAL $Z^{-6} w$ (sec $^{-1}$)	
1	8.2291	2.5371	4.089	8.2291	8.2291
20	8.1181	2.5028	4.098	8.1181	8.1181
40	7.8096	2.4156	4.133	7.8101	7.8101
60	7.3446	2.3024	4.216	7.3476	7.3478
80	6.7440	2.1822	4.392	6.7516	6.7524
92	6.3097	2.1118	4.578	6.3248	6.3265

TABLE 19
Total and two-E1 Integrated Decay Rates

of the $2s_{\frac{1}{2}}$ Metastable State in Hydrogenic Ions

Z	w _{2E1} (sec ⁻¹)	w _{total} (sec ⁻¹)
1	8.2291	8.2291
2	5.2661 (2)	5.2661 (2)
3	5.9973 (3)	5.9973 (3)
4	3.3689 (4)	3.3689 (4)
5	1.2847 (5)	1.2847 (5)
6	3.8347 (5)	3.8347 (5)
7	9.6654 (5)	9.6654 (5)
8	2.1525 (6)	2.1525 (6)
9	4.3612 (6)	4.3612 (6)
10	8.2010 (6)	8.2010 (6)
11	1.4518 (7)	1.4518 (7)
12	2.4451 (7)	2.4451 (7)
13	3.9491 (7)	3.9491 (7)
14	6.1547 (7)	6.1547 (7)
15	9.3017 (7)	9.3017 (7)
16	1.3686 (8)	1.3686 (8)
17	1.9668 (8)	1.9668 (8)
18	2.7682 (8)	2.7682 (8)
19	3.8242 (8)	3.8242 (8)
20	5.1956 (8)	5.1956 (8)

Table 19 continued

Z	w _{2E1} (sec ⁻¹)	w _{total} (sec ⁻¹)
21	6.9530 (8)	6.9530 (8)
22	9.1785 (8)	9.1785 (8)
23	1.1966 (9)	1.1966 (9)
24	1.5423 (9)	1.5423 (9)
25	1.9672 (9)	1.9672 (9)
26	2.4850 (9)	2.4850 (9)
27	3.1111 (9)	3.1111 (9)
28	3.8627 (9)	3.8628 (9)
29	4.7591 (9)	4.7592 (9)
30	5.8215 (9)	5.8217 (9)
32	8.5402 (9)	8.5405 (9)
34	1.2235 (10)	1.2236 (10)
36	1.7164 (10)	1.7164 (10)
40	3.1988 (10)	3.1990 (10)
42	4.2647 (10)	4.2651 (10)
45	6.3994 (10)	6.4003 (10)
50	1.1867 (11)	1.1869 (11)
56	2.2972 (11)	2.2980 (11)
60	3.4267 (11)	3.4282 (11)
65	5.4353 (11)	5.4387 (11)
70	8.3070 (11)	8.3139 (11)
74	1.1392 (12)	1.1404 (12)

Table 19 continued

Z	w_{2E1} (sec $^{-1}$)	w_{total} (sec $^{-1}$)
80	1.7676 (12)	1.7701 (12)
85	2.4778 (12)	2.4824 (12)
90	3.3939 (12)	3.4021 (12)
92	3.8259 (12)	3.8361 (12)
100	5.9814 (12)	6.0045 (12)
110	9.7564 (12)	9.8152 (12)

found by Johnson⁷. The difference between the results becomes larger for larger values of Z . The reason for this difference is that Johnson's results are calculated in the long-wavelength approximation, i.e., taking into account only the contribution of the j_{L-1} term in (6.17). The method used by Johnson is described in Appendix C. Eliminating from (6.17) the contribution of the j_L and j_{L+1} terms in our calculations, we could reproduce Johnson's results. A comparison between the exact values of the total decay rate for two-E1 transitions and those obtained in the long-wavelength approximation is presented in Table 20.

In the range $1 \leq Z \leq 92$, the Z dependence of the total decay rate is approximated by

$$Z^{-6} w_{\text{total}} (\text{s}^{-1}) = 8.22943 \frac{[1 + 3.9448 (\alpha Z)^2 - 2.040 (\alpha Z)^4]}{[1 + 4.6019 (\alpha Z)^2]}$$

$$Z^{-6} w_{\text{2E1}} (\text{s}^{-1}) = 8.22943 \frac{[1 + 4.2770 (\alpha Z)^2 - 2.240 (\alpha Z)^4]}{[1 + 4.9346 (\alpha Z)^2]}$$

In both cases, the average standard deviation in the approximation, is $1.7 \cdot 10^{-4}$.

In the range $1 \leq Z \leq 20$, an interpolation yields

$$Z^{-6} w (\text{s}^{-1}) = 8.22937 \frac{[1 + 0.61898 (\alpha Z)^2]}{[1 + 1.27116 (\alpha Z)^2]}$$

with an average standart deviation in $Z^{-6} w$ of $1.3 \cdot 10^{-5}$.

Finally, concerning the gauge invariance of the results, we found that the difference in the differential decay rate for $G=0$ and $G=(2)^{1/2}$

TABLE 20

Comparison Between the Long Wavelength Approximation
and the Exact Values of the two-E1 Total Decay Rates

Z	L. W. ⁷	EXACT	RELATIVE
	Z^{-6} w(2E1)	Z^{-6} w(2E1)	ERROR
1	8.2290	8.2291	0.001 %
20	8.0825	8.1181	0.44 %
50	7.5713	7.5949	3.0 %
92	5.6287	6.3097	11 %

was less than $10^{-5}\%$ for $Z = 1$ and less than $5 \times 10^{-3}\%$ for $Z = 92$. We found that the differences between the $G=0$ and $G=2^{\frac{1}{2}}$ values would become smaller as the size of the basis set was increased. As an example, in Figure 13 we plot $\gamma(0.5, 92)$ as a function of $N^{-\frac{1}{2}}$, where N is the dimension of the basis set. We note that the values for $G=2^{\frac{1}{2}}$ converge much faster than those for $G=0$. Due to this fast convergence, all the results presented were obtained with $G=2^{\frac{1}{2}}$ and with a basis set that consisted of fourteen (twice) basis vectors.

Relativistic Sum Over Oscillator Strengths

We calculate in this section the positive energy contribution to the relativistic dipole oscillator strength sum rule with retardation, for the ground state of hydrogenic ions.

This sum has been previously estimated to be approximately between 0.82 and 0.87 for lead¹³. According to our results, this value should be 0.7195.

Using the notation in (6.35), the oscillator strength sum rule can be written as

$$S = \frac{1}{2\pi(j_0+1)} \sum_{\substack{j, n_j \\ (\epsilon_{n_j} > 0) \\ m_i, m_f}} \frac{c^2}{\omega_{n_j}} \sum_M (-i)^M \langle m_f | \tilde{\alpha}_{LM}^{(n_j)} | n_j \rangle \langle n_j | \tilde{\alpha}_{LM}^{(n_i)} | m_i \rangle \quad (6.47)$$

where $\omega_{n_j} = E_{n_j} - E_0$.

The summation over M, m_i and m_f gives

$$S = \frac{1}{2\pi(2j_0+1)} \sum_{\epsilon_{n_j} > 0} \frac{c^2}{\omega_{n_j}} \Delta^{LJ} \left| \tilde{M}_{o_{n_j}}(L, J, \omega_{n_j}) \right|^2 \quad (6.48)$$

where

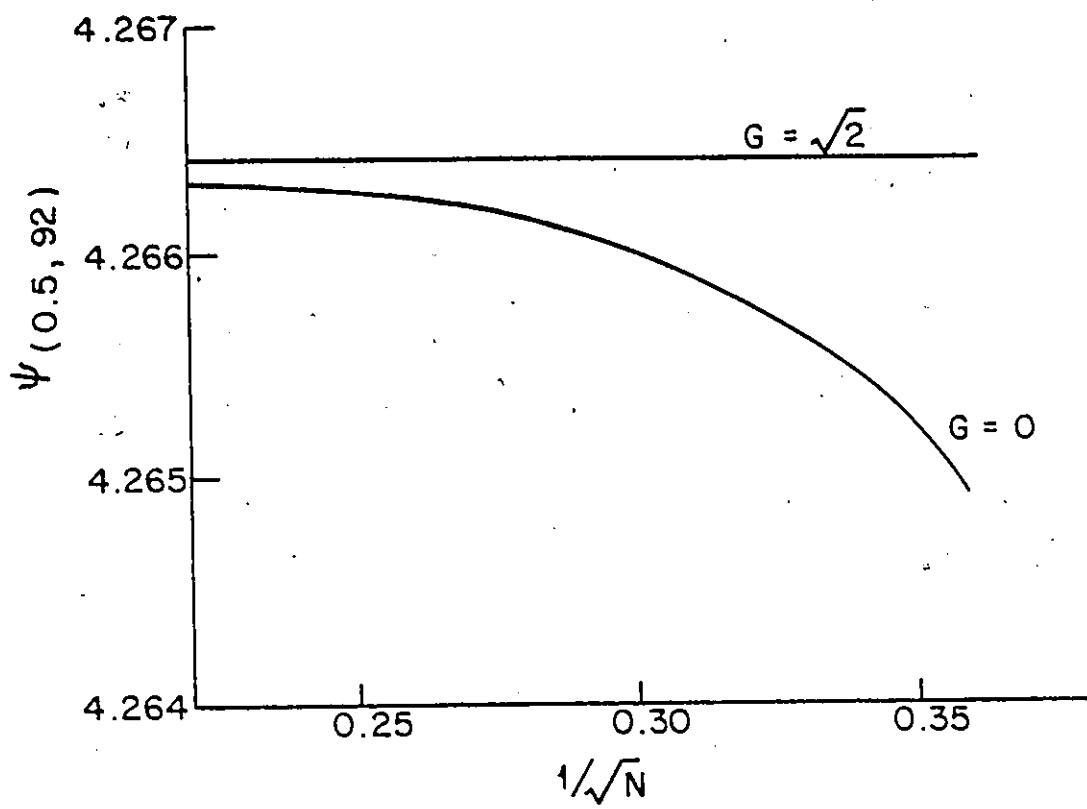


FIGURE 13. Dependence of the differential decay rate on the size of the basis set for two different values of the gauge parameter G .

$$\Delta^{LJ} = 4\pi \frac{(2J+1)}{(2L+1)} \begin{pmatrix} J_0 & L & J \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}. \quad (6.49)$$

In the following we will deal only with electric dipole transitions from the ground state. We note that²⁰

$$\tilde{M}_{0n_J}(1,1,\omega_{n_J}) \xrightarrow[\omega_{n_J}/c \rightarrow 0]{} \sqrt{2} \left(\frac{\omega_{n_J}}{c} \right) \langle 0 | r | n_J \rangle, \quad (6.50)$$

therefore

$$S \xrightarrow[\omega_{n_J}/c \rightarrow 0]{} \frac{2}{3} \sum_{J,n_J} \frac{(2J+1)}{6} \omega_{n_J} |\langle 0 | r | n_J \rangle|^2 = 1. \quad (6.51)$$

We can rewrite (6.48) as

$$S = \frac{1}{3} \sum_J \frac{(2J+1)}{6} \sum_{n_J} f_{0n_J} = \sum_{J,n_J} \bar{f}_{0n_J} \quad (6.52)$$

where \bar{f}_{0n_J} is the oscillator strength given by

$$\bar{f}_{0n_J} = \frac{c^2}{\omega_{n_J}} \left| \tilde{M}_{0n_J}(1,1,\omega_{n_J}) \right|^2 \xrightarrow[\omega_{n_J}/c \rightarrow 0]{} 2\omega_{n_J} |\langle 0 | r | n_J \rangle|^2. \quad (6.53)$$

We perform the integrals occurring in (6.53) in two different ways.

For $\frac{\omega_{n_J}}{c} \lesssim 0.5$ we use, as in (6.44):

$$U_L = \int e^{-\lambda r} r^\gamma j_L \left(\frac{\omega}{c} r \right) dr =$$

$$= \frac{\sqrt{\pi}}{2^{L+1}} \frac{\left(\frac{\omega}{c}\right)^L}{\lambda^{\gamma+L+1}} \frac{\Gamma(\gamma+L+1)}{\Gamma(L+\frac{3}{2})} F \left[\frac{\gamma+L+1}{2}, \frac{\gamma+L+2}{2}; L+\frac{3}{2}; -\left(\frac{\omega}{\lambda c}\right)^2 \right].$$

For $\frac{\omega_{n_1}}{c} > 0.5$, we use

$$U_L = \frac{r(\gamma)}{\lambda^{\gamma+1} \Gamma(1+\gamma^2)^{1/2}} w_L$$

with

$$w_0 = \sin(\gamma\varphi)$$

$$w_1 = \frac{(1+\gamma^2)^{1/2}}{8G} \sin[(\gamma-1)\varphi] - \cos(\gamma\varphi)$$

$$w_2 = \frac{3(1+\gamma^2)}{G^2(\gamma-1)(\gamma-2)} \sin[(\gamma-2)\varphi] - \sin(\gamma\varphi) -$$

$$-\frac{3(1+\gamma^2)^{1/2}}{G(\gamma-1)} \cos[(\gamma-1)\varphi]$$

where

$$\tilde{\gamma} = \frac{\omega}{\lambda c},$$

$$\varphi = \arctan \tilde{\gamma}.$$

The overlap integrals:

$$O_L = \int_{P_2}^{P_1} j_L \int_{P_1}^{P_2} dr$$

are given by (6.45) for $\frac{\omega}{c} \leq 0.5$, and by

$$v_2 = \frac{B(2,1)}{\delta} \frac{\omega_2}{G(1+\delta^2)^{1/2}}$$

for $\frac{\omega}{c} > 0.5$, where we follow the notation used in (6.45).

In Table 21 we present the results obtained for S for a selected number of values of Z and we compare them with the values obtained without retardation. Both sets of values were obtained with a fourteen vector basis set (twice). The retarded values were obtained for the more rapidly convergent case $G=2^{1/2}$. In the same table we list some values obtained using $G=0$.

In Table 22 we list the results obtained for the "weighted" oscillator strengths \tilde{f}_{n_j} for transitions up to $n_j=7$. These results differ also from those obtained by Levinger et al.¹³, because of the omission in their work of higher order terms in the dipole operator.

In Figure 14 we plot S(Z) with and without retardation.

An interpolation of the retarded values yields

$$S = 1 - 0.963782 (\alpha Z)^2 + 0.75474 (\alpha Z)^4$$

for $1 \leq Z \leq 50$, and

$$S = 1 - 0.921526 (\alpha Z)^2 + 0.39331 (\alpha Z)^4$$

for $1 \leq Z \leq 100$.

Applications to scattering. If we denote by $G_{\text{abs}}(\omega)$ the absorption cross-section and by $G_{\text{s.e.}}(\omega)$ the stimulated emission cross section for a

TABLE 21

Relativistic Dipole Oscillator Strength Sums
with and without Retardation

Z	S (ret) $G = (2)^{1/2}$ ^a	S (ret) $G = 0$	S (no ret.)
1	0.9999485	0.9999485	0.9999556
10	0.99490	0.99489	0.99562
20	0.9798	0.9797	0.9850
30	0.9554		0.9633
40	0.9236		0.9375
50	0.8849	0.8845	0.9065
60	0.8397		0.8710
70	0.7882		0.8314
80	0.7313		0.7878
82	0.7193	0.7176	0.7784
90	0.669		0.7399
100	0.60		0.69

^a G is the gauge parameter.

TABLE 22

Retarded Values of the Oscillator Strengths for Z = 82

N_p	$f_{1/2}$	$f_{3/2}$	TOTAL
2	1.1938916(-1)	1.9332478(-1)	3.1271394(-1)
3	1.9576715(-2)	4.0164378(-2)	5.9741093(-2)
4	6.7419487(-3)	1.4974973(-2)	2.1716921(-2)
5	3.1322687(-3)	7.2287299(-3)	1.0360998(-2)
6	1.7150032(-3)	4.0464573(-3)	5.7614605(-3)
7	1.042664(-3)	2.4954748(-3)	3.5381388(-3)

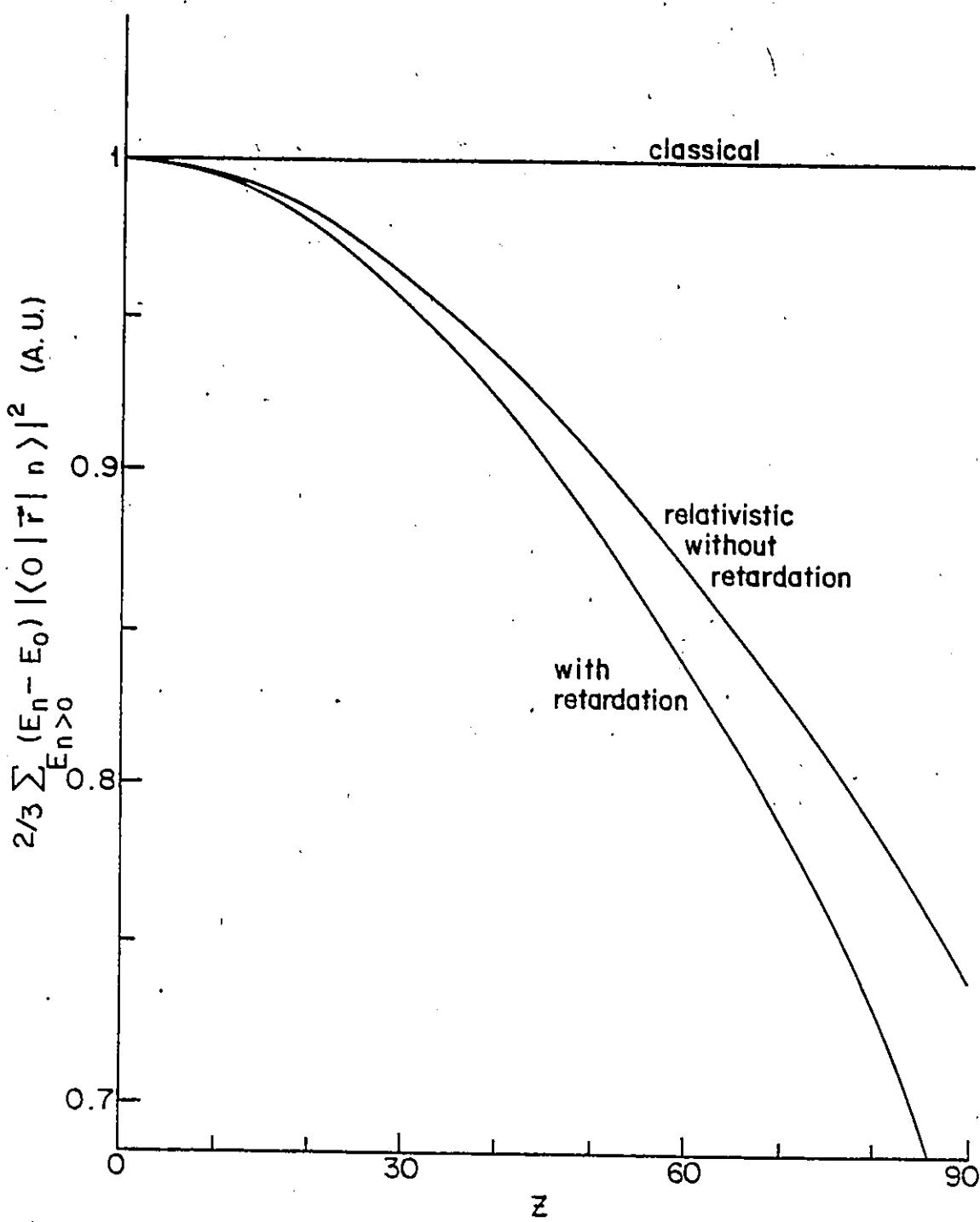


FIGURE 14. Z-dependence of the oscillator strength sum rule with and without retardation.

hydrogenic system exposed to electromagnetic radiation, in the dipole approximation after summing over polarizations, one obtains¹⁸

$$\int_0^\infty [\tilde{\epsilon}_{ab}(\omega) - \tilde{\epsilon}_{s.e.}(\omega)] d\omega = 2\pi^2\alpha S. \quad (6.55)$$

In the non relativistic case, $S = 1$. In the relativistic case, the corrections to (6.55) are given by (6.54).

The straight oscillator strength sum rule can also be used for calculations involving the photoelectric effect. The photoelectric effect cross section can be expressed as:¹¹

$$\tilde{\epsilon}(E) = 2\pi^2\alpha \frac{dS(E)}{dE} \quad (6.56)$$

where

$$S(E) = \sum_{E_i}^E \bar{f}(E)$$

with \bar{f} defined in (6.52).

Denoting by $d\bar{f}(E)$ the average oscillator strength between energy values E and $E + \Delta E$, and by $d\gamma = \Delta E/I$ the energy step ΔE in units of the ionization energy I , we can approximate (6.56) by

$$\tilde{\epsilon}(\gamma) = \frac{2\pi^2\alpha}{I} \frac{d\bar{f}}{d\gamma} = \frac{2\pi^2\alpha}{I} \bar{g}(\gamma) \quad (6.57)$$

This approximation, known as Stieltjes imaging,²² allows one to calculate (6.56) for a set of different energies E_k using the variational basis set.

With these definitions, the Stieltjes value for the oscillator strength density \bar{g} in (6.57) is given by

$$\bar{g}(\bar{\gamma}_k) = \frac{\frac{1}{2}(\bar{\gamma}_k + \bar{\gamma}_{k+1})}{\bar{\gamma}_{k+1} - \bar{\gamma}_k} \quad (6.58a)$$

with

$$\bar{\gamma}_k = \frac{1}{2} (\gamma_k + \gamma_{k+1}). \quad (6.58b)$$

In Figure 15 we plot $\bar{g}_{1/2}(\bar{\gamma}_k)$, $\bar{g}_{3/2}(\bar{\gamma}_k)$ and $\bar{g}_{\text{total}}(\bar{\gamma}_k)$ for lead. From Figure 15, the value of \bar{g} obtained for the ionization limit $\bar{\gamma}=1$ is $\bar{g}_{\text{total}}(1) = 0.61$. This value lies half the way between $\bar{g}(1) = 0.69$ obtained by Payne and Levinger by extrapolation from the discrete energy levels¹³ and $\bar{g}(1) = 0.56$ obtained by Hulme by extrapolation from the continuum.²³

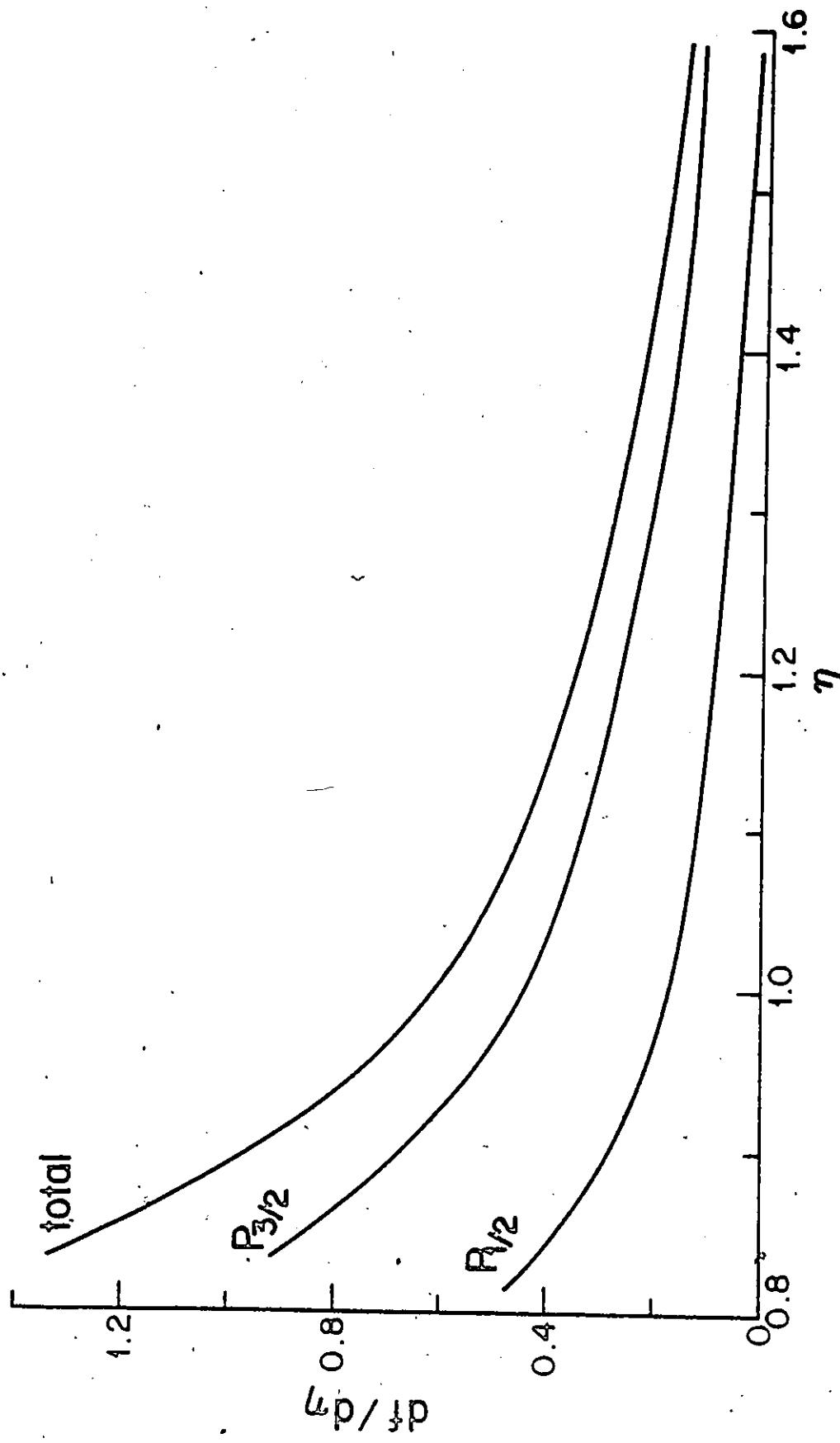


FIGURE 15. Stieltjes values of the oscillator strength density as a function of the energy for Lead.
The energy is measured in units of the ionization energy I .

CHAPTER VII

DISCUSSION

A variational discrete representation of the relativistic energy spectrum of an electron in a Coulomb field has been constructed. We have shown that by a proper choice of the variational basis set, the energy spectrum obtained by the diagonalization of the Dirac Hamiltonian with a Coulomb potential yields a discrete representation of the hydrogenic spectrum including both the positive and negative continua.

We could see that to require the maximum power of r in the large and small components to be the same is a necessary condition for the positive energy solutions to be upper bounds to the ground state, and for the negative energy solutions to be lower bounds to $-mc^2$. If we denote by q the ratio between the radial functions of the large and small components, i.e., $q = g/f$, then this requirement is equivalent to asking q and q^{-1} to be regular for $r \rightarrow \infty$ and for $r \rightarrow 0$, which are conditions satisfied by the exact solutions. That is, asking the number of powers of r in the large and small components to be the same, is equivalent to asking the variational eigenvectors to satisfy the boundary conditions

$$q \xrightarrow[r \rightarrow \infty]{} \text{constant} \neq 0$$
$$q \xrightarrow[r \rightarrow 0]{} \text{constant} \neq 0$$

satisfied by the exact solutions.

We saw also that the calculation of sum rules by means of the variational set yields accurate results, the accuracy being in direct relation to the size of the basis set. This result implies that the variational basis set can be used to represent the Dirac Green's function with an

increasing accuracy as the dimension of the basis set is increased. That is, that the variational space is complete.

With the requirements of boundness and completeness satisfied, the basis set provides a good framework for relativistic calculations involving summations (and integrations) over intermediate states of hydrogenic systems. We note that if only a sum over positive states is required, then we simply omit the negative energy variational eigenvectors.

We used this technique to obtain relativistic results for electric dipole polarizabilities and two-photon emission, calculations that require summations over the complete spectrum, and to obtain results for the straight oscillator strength sum rule by summing over positive states only.

The method is very useful in the sense that it simplifies considerably otherwise very complicated calculations. It is then a powerful technique for the relativistic calculation of atomic properties and scattering cross-sections and provides a natural framework for Q.E.D. calculations. The results obtained in this work, provide a basis for the development of this method to include systems of two or more electrons.

APPENDIX A

Integral Properties of Hydrogenic Bound State Eigenfunctions

Let ψ be an eigenfunction

$$\psi = \begin{pmatrix} i g_r \Omega_{j\ell M} \\ -f_r \Omega_{j\ell M} \end{pmatrix} \quad (\text{A.1})$$

where g and f satisfy

$$g(r) \xrightarrow[r \rightarrow \infty]{} 0, \quad f(r) \xrightarrow[r \rightarrow \infty]{} 0, \quad (\text{A.2})$$

$$g' + \frac{\kappa}{r} g - \left(\alpha E + \frac{\alpha z}{r} + \frac{1}{\alpha} \right) f = 0 \quad (\text{A.3a})$$

$$f' - \frac{\kappa}{r} f + \left(\alpha E + \frac{\alpha z}{r} - \frac{1}{\alpha} \right) g = 0 \quad (\text{A.3b})$$

and

$$\int (g^2 + f^2) dr = 1. \quad (\text{A.3c})$$

Multiplying (A.3a) by g and (A.3b) by f , we obtain

$$g'g + \frac{\kappa}{r} g^2 - \left(\alpha E + \frac{\alpha z}{r} \right) fg - \frac{1}{\alpha} fg = 0 \quad (\text{A.4a})$$

$$f'f - \frac{\kappa}{r} f^2 + \left(\alpha E + \frac{\alpha z}{r} \right) fg - \frac{1}{\alpha} fg = 0. \quad (\text{A.4b})$$

Integrating the sum of equations (A.4) and using the boundary conditions (A.2), we have

$$\kappa \int \frac{dr}{r} (g^2 - f^2) = \frac{2}{\alpha} \int fg dr. \quad (A.5)$$

Multiplying (A.5a) by f and (A.5b) by g , we obtain

$$g'f + \frac{\kappa}{r} gf - \left(E\alpha + \frac{\alpha Z}{r}\right) f^2 - \frac{1}{\alpha} f^2 = 0 \quad (A.6a)$$

$$f'g - \frac{\kappa}{r} fg + \left(E\alpha + \frac{\alpha Z}{r}\right) g^2 - \frac{1}{\alpha} g^2 = 0. \quad (A.6b)$$

Integrating the sum of equations (A.6) and using (A.2) and (A.5c)

$$\alpha E \int (g^2 - f^2) dr + \alpha Z \int \frac{dr}{r} (g^2 - f^2) = \frac{1}{\alpha}. \quad (A.7)$$

Using (A.5), (A.7) becomes

$$\alpha E \int (g^2 - f^2) dr + \frac{\alpha Z}{\kappa} \int fg dr = \frac{1}{\alpha}. \quad (A.8)$$

Multiplying (A.3) by $2r$ and using

$$2rgg' = (rg^2)' - g^2$$

we obtain

$$(rg^2)' - g^2 + 2Kg^2 - 2(\alpha Er + \alpha Z)fg - \frac{2}{\alpha} rfg = 0 \quad (A.9a)$$

$$(r f^2)' - f^2 - 2Kf^2 + 2(\alpha E r + \alpha z) fg - \frac{2}{\alpha} r fg = 0. \quad (\text{A.9b})$$

The integration of the sum and difference of equations (A.9) yields

$$-\frac{4}{\alpha} \int r f g dr + 2K \int (g^2 - f^2) dr = 1 \quad (\text{A.10})$$

$$-\int (g^2 - f^2) dr + 2K - 4\alpha E \int r f g dr - 4\alpha z \int f g dr = 0. \quad (\text{A.11})$$

Using (A.10) into (A.11) we obtain

$$-\int (g^2 - f^2) dr + 2K + \alpha^2 E - 2K\alpha^2 E \int (g^2 - f^2) dr - 4\alpha z \int f g dr = 0.$$

Using (A.8), the last equation results in

$$\int (g^2 - f^2) dr = \alpha^2 E \quad (\text{A.12})$$

which together with

$$\int (g^2 + f^2) dr = 1 \quad (\text{A.3c})$$

yields

$$\int g^2 dr = \frac{1}{2} (1 + \alpha^2 E) \quad (\text{A.13a})$$

$$\int f^2 dr = \frac{1}{2} (1 - \alpha^2 E) \quad (\text{A.13b})$$

Using (A.13), (A.8) becomes

$$\int fg dr = \frac{K}{2\alpha^2} [1 - (\alpha^2 E)^2] \quad (A.14)$$

With these results, (A.10) and (A.6) become

$$\int fg r dr = \frac{\alpha}{4} [2K\alpha^2 E - 1] \quad (A.15)$$

$$\int \frac{dr}{r} (g^2 - f^2) = \frac{1}{\alpha^2 Z} [1 - (\alpha^2 E)^2]. \quad (A.16)$$

Noting that

$$\bar{\psi} = \psi^t \beta$$

equation (A.16) can be rewritten as

$$\int \bar{\psi} V_{out} \psi dr = -\frac{1}{\alpha^2} [1 - (\alpha^2 E)^2].$$

APPENDIX B
Gauge Invariance in Relativistic
Two-Photon Emission Processes

Let the transition operators be of the form

$$\begin{aligned}\hat{A}_a^* &= \beta \left\{ i A_a(\vec{k}_a, \vec{r}) + G_a \left(-i \frac{\vec{\alpha} \cdot (\nabla \varphi_a(\vec{k}_a, \vec{r}))}{k_a} + \varphi_a(\vec{k}_a, \vec{r}) \right) \right\} = \\ &= \beta \left\{ i A_a + G_a A_a^G \right\} \quad (B.1)\end{aligned}$$

where

$$A_a = \vec{\alpha} \cdot \vec{A}_a(\vec{k}_a, \vec{r}),$$

G is the gauge variable, and φ is an arbitrary scalar function of \vec{k} and \vec{r} .

We note first the gauge invariance for a one-photon transition, i.e.

$$\omega = E_i - E_f :$$

$$\begin{aligned}\langle f | A^G | i \rangle &= -\frac{i}{k} \langle f | \vec{\alpha} \cdot (\nabla \varphi) | i \rangle + \langle f | \varphi | i \rangle = \\ &= \frac{1}{\omega} \langle f | [H, \varphi] | i \rangle + \langle f | \varphi | i \rangle = \\ &= \left[1 - \frac{E_i - E_f}{\omega} \right] \langle f | \varphi | i \rangle = 0 \quad (B.2)\end{aligned}$$

where we used

$$-ic\vec{\alpha} \cdot (\nabla \varphi) = [H, \varphi]. \quad (B.3)$$

In the remainder of this appendix, we will alternatively use the following notation

$$\langle f | A_\alpha(\vec{k}_\alpha, \vec{r}) | i \rangle = A_{fi}^{(\alpha)}. \quad (B.4)$$

We are interested in the gauge invariance of the sum

$$S = \sum_n \left\{ \frac{\hat{A}_{fn}^e(2) \hat{A}_{ni}^e(1)}{E_n - E_i + \omega_1} + \frac{\hat{A}_{fn}^e(1) \hat{A}_{ni}^e(2)}{E_n - E_f - \omega_1} \right\} \quad (B.5)$$

with

$$E_i - E_f = \omega = \omega_1 + \omega_2. \quad (B.6)$$

We can rewrite (B.5) as

$$S = S^0 + G_1 S^1 + G_2 S^2 + G_1 G_2 S^{12}. \quad (B.7)$$

Consider now the contribution to S linear in G_1 :

$$S^1 = \sum_n \left\{ \frac{A_{fn}^{(2)} \langle n | \left(-i \frac{\vec{\alpha} \cdot \nabla}{k_1} \varphi_i^{(1)} \right) | i \rangle}{E_n - E_i + \omega_1} + \frac{A_{fn}^{(2)} \varphi_{ni}^{(1)}}{E_n - E_i + \omega_1} + \frac{\langle f | \left(-i \frac{\vec{\alpha} \cdot \nabla}{k_1} \varphi_i^{(1)} \right) | n \rangle A_{ni}^{(2)}}{E_n - E_f - \omega_1} + \frac{\varphi_{fn}^{(1)} A_{ni}^{(2)}}{E_n - E_f - \omega_1} \right\} =$$

$$\begin{aligned}
 &= \frac{1}{\omega_1} \sum_n \left\{ \frac{A_{fn}(2) \langle n | ([H, \varphi_i(1)] + \omega_1 \varphi_i(1)) / i \rangle}{E_n - E_i + \omega_1} + \right. \\
 &\quad \left. + \frac{\langle f | ([H, \varphi_i(1)] + \omega_1 \varphi_i(1)) / n \rangle A_{ni}(2)}{E_n - E_f - \omega_1} \right\} = \\
 &= \frac{1}{\omega_1} \sum_n \left\{ A_{fn}(2) \varphi_{ni}(1) - \varphi_{fn}(1) A_{ni}(2) \right\} = 0.
 \end{aligned}$$

The same applies to S^2 , then, in (B.7) we have

$$S^1 = S^2 = 0. \quad (\text{B.8})$$

Using (B.5), we can write the term in S quadratic in the gauge variables as

$$\begin{aligned}
 S'^2 &= \frac{1}{\omega_1 \omega_2} \sum_n \left\{ \frac{\langle f | [H, \varphi_2(2)] / n \rangle \langle n | ([H, \varphi_1(1)] + \omega_1 \varphi_1(1)) / i \rangle}{E_n - E_i + \omega_1} + \right. \\
 &\quad + \omega_2 \frac{\varphi_{fn}(2) \langle n | ([H, \varphi_1(1)] + \omega_1 \varphi_1(1)) / i \rangle}{E_n - E_i + \omega_1} + \\
 &\quad + \frac{\langle f | ([H, \varphi_1(1)] + \omega_1 \varphi_1(1)) / n \rangle \langle n | [H, \varphi_2(2)] / i \rangle}{E_n - E_f - \omega_1} + \\
 &\quad + \omega_2 \left. \frac{\langle f | ([H, \varphi_1(1)] + \omega_1 \varphi_1(1)) / n \rangle \varphi_{ni}(2)}{E_n - E_f - \omega_1} \right\} =
 \end{aligned}$$

$$\begin{aligned} &= \frac{1}{\omega_1 \omega_2} \sum_n \left\{ (E_f - E_n + \omega_2) \varphi_{fn}(2) \varphi_{ni}(1) - \right. \\ &\quad \left. - (E_n - E_i + \omega_2) \varphi_{pn}(1) \varphi_{ni}(2) \right\}. \end{aligned} \quad (\text{B.9})$$

But

$$\begin{aligned} \sum_n \langle f | \varphi_2(2) | n \rangle \langle n | \varphi_1(1) | i \rangle &= \langle f | \varphi_2(2) \varphi_1(1) | i \rangle = \\ &= \langle f | \varphi_1(1) \varphi_2(2) | i \rangle = \sum_n \langle f | \varphi_1(1) | n \rangle \langle n | \varphi_2(2) | i \rangle, \end{aligned} \quad (\text{B.10})$$

then, (B.9) can be written as

$$\begin{aligned} S^{12} &= \frac{1}{\omega_1 \omega_2} \sum_n \left\{ \langle f | [H, \varphi_2(2)] | n \rangle \langle n | \varphi_1(1) | i \rangle - \right. \\ &\quad \left. - \langle f | \varphi_1(1) | n \rangle \langle n | [H, \varphi_2(2)] | i \rangle \right\} = \\ &= \frac{1}{\omega_1 \omega_2} \langle f | [[H, \varphi_2(2)], \varphi_1(1)] | i \rangle = 0 \end{aligned} \quad (\text{B.11})$$

where we used (B.3).

Then, using (B.8) and (B.11) in (B.7) we obtain finally

$$S = S^o. \quad (\text{B.12})$$

Equation (B.12) shows that the sum S is independent of the gauge parameters.

In the same way, gauge invariance can be demonstrated for any two-photon processes involving emission or absorption of electromagnetic radiation.

APPENDIX C

Electric Dipole Two-Photon Emission in the Long Wavelength Approximation.

From (6.33) and (6.29), we have in the case of two-E1 emission:

$$\frac{d\omega}{d\omega_1} = \frac{\omega_1 \omega_2}{8\pi^3 c^2} \sum_{M_1 M_2} \left| \Theta(2,1) + \Theta(1,2) \right|^2, \quad (C.1)$$

with

$$\Theta(1,2) = \sum_n \frac{\langle f | \vec{a}_{1M_1}^* (\vec{k}_1, \vec{r}) | n \rangle \langle n | \vec{a}_{2M_2}^* (\vec{k}_2, \vec{r}) | i \rangle}{E_n - E_i + \omega_1} \quad (C.2)$$

where $\vec{a}_{1M}^{(1)} = \vec{a}_{1M}^{(2)}$ is given in (6.17a).

Using^{17,1}

$$\frac{c}{\omega} \nabla \left(j_L \left(\frac{\omega}{c} r \right) Y_{LM} \right) = \left(\frac{L+1}{2L+1} \right)^{1/2} j_{L+1} \vec{Y}_{L,L+1,M} + \left(\frac{L}{2L+1} \right)^{1/2} j_{L-1} \vec{Y}_{L,L-1,M}, \quad (C.3)$$

we can rewrite (6.17a) as

$$\vec{a}_{LM}^{(1)} = -i \left(\frac{L+1}{L} \right)^{1/2} \frac{c}{\omega} \nabla \phi_{LM} + \left(\frac{2L+1}{L} \right)^{1/2} i^{L+1} j_{L+1} \left(\frac{\omega}{c} r \right) Y_{L,L+1,M} \cdot 4\pi, \quad (C.4)$$

where

$$\phi_{LM} = i^L j_L \left(\frac{\omega}{c} r \right) Y_{L,M} \cdot 4\pi. \quad (C.5)$$

In the long wavelength approximation, we can neglect the second

term in (C.4), remaining for the electric dipole case:

$$\vec{Q}_{1M}^{(4)} \approx -i\sqrt{2} \frac{c}{\omega} \nabla \phi_M. \quad (C.6)$$

Using now

$$-ic \vec{\alpha} \cdot (\nabla \phi_M) = [H, \phi_M]$$

we obtain in (C.1)

$$\omega_1 \omega_2 [\Theta(2,1) + \Theta(1,2)] = \sum_n \left\{ \frac{(E_f - E_n)(E_n - E_i)}{E_n - E_f - \omega_1} \langle f | \phi_{H_2}^{(4)} | n \rangle \langle n | \phi_{H_2}^{(2)} | i \rangle + \right.$$

$$\left. + \frac{(E_f - E_n)(E_n - E_i)}{E_n - E_i + \omega_1} \langle f | \phi_{H_2}^{(2)} | n \rangle \langle n | \phi_{H_2}^{(4)} | i \rangle \right\} =$$

$$= \sum_n \left\{ -(E_n - E_i) \phi_{fn}^{(4)} \phi_{ni}^{(2)} + (E_f - E_n) \phi_{fn}^{(2)} \phi_{ni}^{(4)} - \right.$$

$$\left. - \frac{\omega_1 (E_n - E_i)}{E_n - E_f - \omega_1} \phi_{fn}^{(4)} \phi_{ni}^{(2)} + \frac{\omega_1 (E_n - E_f)}{E_n - E_i + \omega_1} \phi_{fn}^{(2)} \phi_{ni}^{(4)} \right\} =$$

$$= \langle f | [[H, \phi^{(2)}], \phi^{(4)}] | i \rangle + \sum_n \left[\left[\frac{-\omega_1 (E_n - E_i + \omega_2)}{E_n - E_i + \omega_2} + \frac{\omega_1 \omega_2}{E_n - E_i + \omega_2} \right] \phi_{fn}^{(4)} \phi_{ni}^{(2)} + \right.$$

$$\left. + \left[\frac{\omega_1 (E_n - E_f - \omega_2)}{E_n - E_f - \omega_2} + \frac{\omega_1 \omega_2}{E_n - E_f - \omega_2} \right] \phi_{fn}^{(2)} \phi_{ni}^{(4)} \right].$$

Then, in the long wavelength approximation, we have

$$\Theta(2,1) + \Theta(1,2) = \sum_{n_3} \left\{ \frac{\langle f | \phi_{H_1}(z) | n \rangle \langle n | \phi_{H_2}(z) | i \rangle}{E_n - E_i + \omega_3} + \frac{\langle f | \phi_{H_2}(z) | n \rangle \langle n | \phi_{H_1}(z) | i \rangle}{E_n - E_i + \omega_3} \right\}. \quad (C.6)$$

An outline of the method used by Johnson⁷ to deal with the matrix elements in (C.6), is the following. If ψ^j is defined by the linear combination

$$|\psi^j(\omega_i)\rangle = \sum_{n_j} |n_j\rangle \frac{\langle n_j | \phi_{H_1}(z) | i \rangle}{E_{n_j} - E_i + \omega_i} \quad (C.7)$$

then, in (C.6)

$$\Theta(2,1) + \Theta(1,2) = \sum_j \left\{ \langle f | \phi_{H_1}(z) | \psi^j(\omega_2) \rangle + \langle f | \phi_{H_2}(z) | \psi^j(\omega_1) \rangle \right\}. \quad (C.8)$$

Applying the Dirac Hamiltonian to (C.7), we obtain

$$(H - E_i + \omega_i) |\psi^j(\omega_i)\rangle = \phi_{H_1}^j(z) |i\rangle. \quad (C.9)$$

We use the notation

$$|\psi^j\rangle = \begin{pmatrix} i \frac{S_j}{r} \mathcal{Q}_{j1M} \\ -\frac{T_j}{r} \mathcal{Q}_{j1M} \end{pmatrix}. \quad (C.10)$$

Using (C.9), the radial functions in (C.10) obey the coupled equations:

$$\left(\frac{1}{\alpha^2} + V - E_i + \omega_i\right) S_J - \frac{i}{\alpha} \left(\frac{d}{dr} - \frac{K}{r}\right) T_J = j_{1H_i} \left(\frac{\omega}{c} r\right) g_i(r) \quad (C.11a)$$

$$\frac{i}{\alpha} \left(\frac{d}{dr} + \frac{K}{r}\right) S_J - \left(\frac{1}{\alpha^2} - V + E_i - \omega_i\right) T_J = j_{1H_i} \left(\frac{\omega}{c} r\right) f_i(r). \quad (C.11b)$$

After factoring out the angular matrix elements in (C.1), only the radial contribution is needed. A numerical integration of system (C.11) yields S_J and T_J . Then, another numerical integration in (C.8) with S_J and T_J known, yields the radial contribution to $\Theta(2,1) + \Theta(1,2)$.

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