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Atomic fine structure in a space of constant curvature

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Abstract. As a contribution to a tentative formulation of atomic physics in a curved space, the determination of atomic fine structure energies in a space of constant curvature is investigated. Starting from the Dirac equation in a curved space–time, the analogue of the Pauli equation in a general coordinate system is derived. When particularising these results to the model of a spherical three-space with a Coulombic field, one obtains the 'curved' form of the one-electron fine structure Hamiltonian, i.e. the curved form of the Landé spin–orbit interaction and of the relativistic correction of the kinetic energy as well as some additional terms which vanish at the traditional flat limit. The theoretical curvature induced shifts and splittings of the fine structure energy levels are put in evidence and examined for the particular case of the hydrogenic $n = 2$ levels.

1. Introduction

In a previous paper (Bessis and Bessis 1979, to be referred to as I), we have suggested the interest of calculating electronic wavefunctions in a space of constant curvature. These calculations have been performed within the framework of a simplistic 'curved orbital' model. In that model, the usual flat Euclidean space is substituted by a spherical three-space which can be viewed as the three-dimensional hypersphere of radius R embedded in a Euclidean four-space. After introducing hyperspherical coordinates (χ, θ, ϕ) in lieu of the polar coordinates (r, θ, ϕ), and the 'curved' form $(1/R)\cot\chi$ of the Coulomb potential, exact solutions of the one-electron Schrödinger equation have been obtained. Within the usual independent particle framework these one-electron wavefunctions can be considered as 'curved orbitals' and can be used as a basis set in order to build up many-electron 'curved' wavefunctions. A multipolar expansion of the bielectronic repulsion potential has been obtained, allowing the computation of the two-electron repulsion integrals as well as further consideration of higher multipolar electrostatic interactions. As expected, one finds again the usual flat results at the asymptotic flat limit, i.e. when $R \to \infty$, $\chi \to 0$ such that $\chi R = r$ remains finite. Although this over-simple model could not be considered as quite satisfactory by the general relativity theorist, nevertheless it seems to us that it could be useful to put in evidence some results due to the closeness of the universe, which cannot be formulated from the asymptotic flat limit. Moreover, from a practical computational point of view, it could be advantageous to transform the radial variable r, with infinite range $[0, \infty[$ of the flat space into an angular variable χ with finite range $(0, \pi)$. This last point remains to be thoroughly investigated.

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In this paper, this 'curved orbitals' model is extended to the consideration of the one-electron spin-dependent interactions, i.e. to the determination of the 'curved' form of the fine structure Hamiltonian (Landé spin–orbit interaction). As is usually done, in order to obtain these terms, one could start from the Dirac equation and then go to the non-relativistic limit via the Pauli equation. Since our working space is now a curved space–time instead of the usual flat space–time, one has to consider a generalised form of the Dirac first-order equation for the electron which is valid in a Riemannian space of four dimensions.

The Dirac equation in a curved space was formulated a long time ago (Tetrode 1928, Fock 1929, Fock and Ivanenko 1929) and has been reinvestigated or reviewed by several authors (see, for instance, Schrödinger 1932, Taub 1937, Pagels 1965, Chapman and Leiter 1976). More recent works also question the possibilities of observing gravitational induced phenomena and, in particular, study the energy levels of a one-electron atom in a curved space–time (Tourrenc and Grossiord 1976, Audretsch and Schäfer 1978, Parker 1980). Let us mention that our approach is different from these last works since one of our motivating purposes is to render tractable atomic fine structure calculations in a spherical three-space on the basis of the 'hydrogenic curved orbitals'. For their part, Tourrenc and Parker have used 'flat' space–time solutions of the Schrödinger and Dirac equations as a basis for calculating curvature contributions to the energy levels by first-order perturbation theory. Therefore one cannot extract from their results the expression of the spherical three-space fine structure Hamiltonian we need. It should be noted that, when expanding our expressions of the fine structure energies in powers of R^{-2}, one should obtain a first-order (in R^{-2}) expression of the curvature effects which can be compared with the non-relativistic one given by Tourrenc and Grossiord (1976) and Parker (1980). In other words, in the above quoted works, the 'master' equation is the Dirac equation in an arbitrary curved space–time in order to put in evidence the curvature corrections to the 'flat' energies, while our point of view is more pragmatic: we consider the Pauli equation in a curved space (and in particular in a spherical three-space), as our 'master' equation, and consequently our results should involve some more curvature effects, even though they are formulated within a non-relativistic scheme. In § 2, the Dirac equation in a curved space–time is used as a starting point in order to derive the Pauli equation in a spherical three-space; special attention is paid to the choice of the Dirac matrices leading to the traditional (θ, ϕ) dependence of the relativistic atomic wavefunctions. A covariant formulation of the Pauli equation is given (§ 3). When particularising these results to the spherical three-space containing a Coulombic field, one obtains the spin-dependent one-electron terms of the Hamiltonian, i.e. the curved form of the Landé interaction as well as some additional terms arising from spin and curvature interaction (§ 4).

2. Dirac equation in spherical three-space

The generally covariant form of the Dirac equation in a curved† space–time of metric $g_{\mu\nu}(x)$ is

$$(ic\hbar\tilde{\gamma}^{\mu}(x)\hat{\nabla}_{\mu} - mc^2)\psi(x) = 0 \tag{1}$$

† The ~ symbol denotes matrices of the curved space–time.

where ψ is a four-component spinor, $\mu = 0, 1, 2, 3$ and the Einstein summation convention is used. $x = (x^0, x^1, x^2, x^3)$.

The $\tilde{\gamma}^\mu(x)$ are coordinate-dependent matrices which obey the anticommutation relations

$$\tilde{\gamma}^\mu(x)\tilde{\gamma}^\nu(x) + \tilde{\gamma}^\nu(x)\tilde{\gamma}^\mu(x) = 2g^{\mu\nu}(x). \tag{2}$$

The spin covariant derivatives of a spinor and of a matrix are, respectively,

$$\hat{\nabla}_\mu\psi = \partial\psi/\partial x^\mu + \mathrm{i}[(e/\hbar c)A_\mu + \Gamma_\mu]\psi, \qquad \hat{\nabla}_\mu B_{\nu\rho}\ldots = B_{\nu\rho\ldots;\mu} + \mathrm{i}[\Gamma_\mu, B_{\nu\rho}\ldots], \tag{3}$$

where ; μ stands for the covariant derivative, the Γ_μ are the Fock–Ivanenko matrices and the A_μ are the electromagnetic four-vector components.

The covariant derivative of a vector ϕ^ν is defined in terms of the Christoffel symbols

$$\phi^\nu{}_{;\mu} = \partial\phi^\nu/\partial x^\mu + \Gamma^\nu_{\alpha\mu}\phi^\alpha, \qquad \phi_{\nu;\mu} = \partial\phi_\nu/\partial x^\mu - \Gamma^\alpha_{\nu\mu}\phi_\alpha, \tag{4}$$

where, following from the vanishing condition $g_{\nu\mu;\alpha} = 0$, the Christoffel symbols are

$$\Gamma^\nu_{\alpha\mu} = \tfrac{1}{2}g^{\nu\rho}(\partial g_{\alpha\rho}/\partial x^\mu + \partial g_{\mu\rho}/\partial x^\alpha - \partial g_{\alpha\mu}/\partial x^\rho), \qquad \Gamma^\nu_{\alpha\mu} = \Gamma^\nu_{\mu\alpha}. \tag{5}$$

The Fock–Ivanenko matrices Γ_μ are obtained from the vanishing condition

$$\hat{\nabla}_\mu\tilde{\gamma}_\nu = \tilde{\gamma}_{\nu;\mu} + \mathrm{i}[\Gamma_\mu, \tilde{\gamma}_\nu] = 0 \tag{6}$$

and are given by the expression

$$\Gamma_\mu = -\tfrac{1}{4}\mathrm{i}\tilde{\gamma}^\nu\tilde{\gamma}_{\nu;\mu}. \tag{7}$$

In view of the further derivation of the Pauli equation in a spherical three-space which leads to the classical Pauli representation flat limit, it is worthwhile to review briefly a convenient representation of the Dirac equation in a spherical three-space.

When introducing hyperspherical coordinates, the space–time line element (Einstein metric) is

$$\mathrm{d}s^2 = c^2\,\mathrm{d}t^2 - R^2\,\mathrm{d}\chi^2 - R^2\sin^2\chi\,(\mathrm{d}\theta^2 + \sin^2\theta\,\mathrm{d}\phi^2) \tag{8}$$

where θ and ϕ lie within their traditional flat bounds $0 \leqslant \phi \leqslant 2\pi$, $0 \leqslant \theta \leqslant \pi$ and $0 \leqslant \chi \leqslant \pi$. Setting $R \to \infty$, $\chi \to 0$ such that $R\chi = r$ remains finite, the spatial part of the line element (8) reduces to that of Euclidean space in which r, θ, ϕ are the usual polar coordinates.

It is easily found that a convenient choice of the Dirac matrices $\tilde{\gamma}^\mu(x)$ which obey the anticommutation relations (2) and lead to the usual polar dependence (θ, ϕ) of the Dirac wavefunction is

$$\begin{aligned}
\tilde{\gamma}^0 &= \gamma^0, \\
\tilde{\gamma}^1 &= (1/R)(\gamma^1\sin\theta\cos\phi + \gamma^2\sin\theta\sin\phi + \gamma^3\cos\theta), \\
\tilde{\gamma}^2 &= (R\sin\chi)^{-1}(\gamma^1\cos\theta\cos\phi + \gamma^2\cos\theta\sin\phi - \gamma^3\sin\theta), \\
\tilde{\gamma}^3 &= (R\sin\chi\sin\theta)^{-1}(-\gamma^1\sin\phi + \gamma^2\cos\phi),
\end{aligned} \tag{9}$$

where the γ^μ are the constant Dirac matrices

$$\begin{aligned}
&\gamma^0 = \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \qquad \gamma^k = \begin{pmatrix} 0 & \sigma^k \\ -\sigma^k & 0 \end{pmatrix}, \qquad k = 1, 2, 3, \\
&I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma^2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\end{aligned} \tag{10}$$

These constant Dirac matrices γ^μ obey the anticommutation relations (2) where $g^{\mu\nu}$ is the Lorentz diagonal constant metric $(1, -1, -1, -1)$.

From the above definitions (see equations (8), (9)) the non-vanishing Christoffel symbols and the Fock–Ivanenko matrices in a curved space–time with line element (8) are found to be

$$\Gamma^1_{22} = -\sin\chi\cos\chi, \qquad \Gamma^1_{33} = -\sin\chi\cos\chi\sin^2\theta, \qquad \Gamma^2_{33} = -\sin\theta\cos\theta,$$
$$\Gamma^2_{12} = \Gamma^2_{21} = \Gamma^3_{13} = \Gamma^3_{31} = \cot\chi, \qquad \Gamma^3_{23} = \Gamma^3_{32} = \cot\theta, \tag{11}$$
$$\Gamma_0 = \Gamma_1 = 0, \qquad \Gamma_k = \frac{\mathrm{i}}{2}\left(\frac{1-\cos\chi}{\sin\chi}\right)\tilde{\gamma}_k\tilde{\gamma}^1 \qquad \text{for } k = 2, 3.$$

One obtains the following expression of the Dirac equation in a spherical three-space $(x^\mu = ct, \chi, \theta, \phi)$:

$$\left[\tilde{\gamma}^\mu\left(\mathrm{i}\frac{\partial}{\partial x^\mu} - \frac{e}{\hbar c}A_\mu\right) - \mathrm{i}\left(\frac{1-\cos\chi}{\sin\chi}\right)\tilde{\gamma}^1 - \frac{mc}{\hbar}\right]\psi = 0. \tag{12}$$

Let us consider the stationary states. Setting

$$\psi = \exp(-\mathrm{i}E_\mathrm{T}t/\hbar), \qquad E_\mathrm{T} = mc^2 + E, \tag{13}$$

and multiplying (12) by $-\gamma^0$, one gets the Dirac equation for stationary states with a scalar potential $A_0 = V$

$$\left[-\frac{\mathrm{i}}{R}\alpha_\chi\left(\frac{\partial}{\partial\chi} + \frac{\cos\chi}{\sin\chi} - \frac{1}{\sin\chi}\right) - \frac{\mathrm{i}}{R\sin\chi}\left(\alpha_\theta\frac{\partial}{\partial\theta} + \frac{\alpha_\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right) + \frac{mc}{\hbar}\beta - \frac{E_\mathrm{T} - eV}{\hbar c}\right]\Phi = 0$$

or alternatively

$$\left[\alpha_\chi\left(p_\chi + \frac{\mathrm{i}\beta}{R\sin\chi}\hat{K}\right) + \frac{mc}{\hbar}\beta - \frac{E_\mathrm{T} - eV}{\hbar c}\right]\Phi(\chi, \theta, \phi) = 0 \tag{14}$$

where

$$p_\chi = -\frac{\mathrm{i}}{R\sin\chi}\frac{\partial}{\partial\chi}\sin\chi, \qquad \hat{K} = \beta\left[1 - \alpha_\chi\left(\alpha_\theta\frac{\partial}{\partial\theta} + \frac{\alpha_\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right)\right] = \beta(1 + \boldsymbol{\sigma}\cdot\boldsymbol{l}),$$

$\boldsymbol{\sigma} = (\sigma^1, \sigma^2, \sigma^3)$ and $\boldsymbol{l}$ is the usual orbital angular momentum,

$$\alpha_\chi = (\alpha_1\cos\phi + \alpha_2\sin\phi)\sin\theta + \alpha_3\cos\theta,$$
$$\alpha_\theta = (\alpha_1\cos\phi + \alpha_2\sin\phi)\cos\theta - \alpha_3\sin\theta,$$

$\alpha_\phi = -\alpha_1\sin\phi + \alpha_2\cos\phi$, $\beta = \gamma^0$, $\alpha_k = \gamma^0\gamma^k$ are the standard Dirac matrices.

At the asymptotic flat limit, it can be easily verified that $p_\chi \to p_r = -(\mathrm{i}/r)(\partial/\partial r)r$; and one finds again the usual flat space expression of the Dirac equation in polar coordinates (see, for instance, Messiah 1964)

$$\left[\alpha_r\left(p_r + \frac{\mathrm{i}\beta}{r}\hat{K}\right) + \frac{mc}{\hbar}\beta - \frac{E_\mathrm{T} - eV}{\hbar c}\right]\Phi(r, \theta, \phi) = 0, \qquad \alpha_r = \alpha_\chi. \tag{15}$$

The resolution of the Dirac equation (14) as well as a possible relativistic formulation of the fine and hyperfine interactions in a spherical three-space will be considered

in a further paper. In the present paper we shall limit ourselves to fine structure calculations within the non-relativistic 'curved' model which have been introduced in paper I and use the curved form of the Pauli equation.

3. Pauli equation in a curved space

Let us consider the Dirac equation (1) in a curved space–time with line element $ds^2 = c^2\,dt^2 - ds_0^2$. For stationary states, the Dirac equation (1) reduces to

$$[i\hbar\tilde{\gamma}^k\hat{\nabla}_k + (1/c)(E_T - eV)\tilde{\gamma}^0 - mc]\Phi = 0 \qquad \text{where } k = 1, 2, 3. \tag{16}$$

Since the $\tilde{\gamma}^\mu(x)$ matrices of the curved space–time are linearly related to the Dirac matrices of the flat space–time, one can write

$$\tilde{\gamma}^0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \qquad \tilde{\gamma}^k(x) = \begin{pmatrix} 0 & \tilde{\sigma}^k(x) \\ -\tilde{\sigma}^k(x) & 0 \end{pmatrix} \tag{17}$$

where the $\tilde{\sigma}^k(x)$ are 2×2 matrices which obey, as well as the $\tilde{\gamma}^k(x)$, the anticommutation rules $\tilde{\sigma}^k\tilde{\sigma}^l + \tilde{\sigma}^l\tilde{\sigma}^k = 2g^{kl}(x)$, $(k, l = 1, 2, 3)$. Consequently

$$\Gamma_k = \begin{pmatrix} \Gamma'_k & 0 \\ 0 & \Gamma'_k \end{pmatrix} \qquad \text{where } \Gamma'_k = -\tfrac{1}{4}i\tilde{\sigma}^l\tilde{\sigma}_{l;k}.$$

Setting $\Phi = \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$, one obtains a couple of equations

$$(E - eV)\Phi_1 + ic\hbar\tilde{\sigma}^k\hat{\nabla}'_k\Phi_2 = 0, \qquad ic\hbar\tilde{\sigma}^k\hat{\nabla}'_k\Phi_1 + (E - eV + 2mc^2)\Phi_2 = 0, \tag{18a, b}$$

where

$$\hat{\nabla}'_k\Phi_j = \partial\Phi_j/\partial x^k + i[(e/\hbar c)A_k + \Gamma'_k]\Phi \qquad j = 1, 2.$$

From inspection of equation (18*b*), it is seen that Φ_2 can be identified with the traditional small component. It is related to the large component Φ_1 by

$$\Phi_2 = -\frac{i\hbar}{2mc}Q(x)\tilde{\sigma}^k\hat{\nabla}'_k\Phi_1 \qquad \text{where } Q(x) = \left(1 + \frac{E - eV(x)}{2mc^2}\right)^{-1}. \tag{19}$$

When going to the non-relativistic limit of the Dirac equation in a curved space–time, the possibility of separation between small and large components implies conditions on the order of magnitude of the curvature radius. For the case of the hydrogenic free atoms, this point has been analysed by Parker (1980) and we shall assume that these conditions are fulfilled.

After substituting for Φ_2 from (19) into equation (18*a*), one obtains the following 'curved' Pauli equation:

$$[(\hbar^2/2m)(\tilde{\sigma}^k\hat{\nabla}'_k)Q(\tilde{\sigma}^l\hat{\nabla}'_l) + E - eV]\Phi_1 = 0. \tag{20}$$

When working out the first term of the equation (20), since $[\tilde{\sigma}^k\hat{\nabla}'_k, Q] = \tilde{\sigma}^k\,\partial Q/\partial x^k$, one obtains

$$\{(\hbar^2/2m)[Q(\tilde{\sigma}^k\hat{\nabla}'_k)(\tilde{\sigma}^l\hat{\nabla}'_l) + \tilde{\sigma}^k\tilde{\sigma}^l(\partial Q/\partial x^k)\hat{\nabla}'_l] + E - eV\}\Phi_1 = 0. \tag{21}$$

Using the commutation properties (Schrödinger 1932)

$$[\tilde{\sigma}^k, \hat{\nabla}'_k] = \frac{\partial \log\sqrt{g}}{\partial x^l}\tilde{\sigma}^l, \qquad [S^{kl}, \hat{\nabla}'_k] = \frac{\partial \log\sqrt{g}}{\partial x^m}S^{ml}, \tag{22}$$

where $S^{kl}=\frac{1}{2}[\tilde{\sigma}^k,\tilde{\sigma}^l]=\tilde{\sigma}^k\tilde{\sigma}^l-g^{kl}$, one gets

$$\begin{aligned}&(\tilde{\sigma}^k\hat{\nabla}'_k)(\tilde{\sigma}^l\hat{\nabla}'_l)=g^{-1/2}\hat{\nabla}'_k(\sqrt{g}g^{kl}\hat{\nabla}'_l)+\tfrac{1}{2}S^{kl}[\hat{\nabla}'_k,\hat{\nabla}'_l],\\&[\hat{\nabla}'_k,\hat{\nabla}'_l]=\tfrac{1}{4}S_{mn}R^{mn}{}_{kl}+(ie/\hbar c)(\partial A_l/\partial x^k-\partial A_k/\partial x^l),\end{aligned}\tag{23}$$

where $R^{mn}{}_{kl}$ is the Riemann curvature tensor and $g=\det|g_{kl}|$.

Finally, the Pauli equation in a curved space becomes, in atomic units,

$$\begin{aligned}\{&-\tfrac{1}{2}g^{-1/2}\hat{\nabla}'_k(\sqrt{g}g^{kl}\hat{\nabla}'_l)-\tfrac{1}{16}S^{kl}S_{mn}R^{mn}{}_{kl}-\tfrac{1}{4}i\alpha S^{kl}F_{kl}\\&-\tfrac{1}{4}\alpha^2Q[\tilde{\sigma}^k\tilde{\sigma}^l(\partial V/\partial x^k)\hat{\nabla}'_l]-(E-V)-\tfrac{1}{2}\alpha^2(E-V)^2\}\Phi_1=0\end{aligned}\tag{24}$$

where $\alpha=e^2\hbar/c$ is the fine structure constant and $F_{kl}=\partial A_l/\partial x^k-\partial A_k/\partial x^l$ is the covariant field magnetic tensor.

It is easily found that this last equation can be rearranged in the form

$$\begin{aligned}\Big[&-\frac{1}{2}\frac{1}{\sqrt{g}}\Big(\frac{\partial}{\partial x^k}+i\alpha A_k\Big)\sqrt{g}g^{kl}\Big(\frac{\partial}{\partial x^l}+i\alpha A_l\Big)-\frac{i}{4}\alpha S^{kl}F_{kl}\\&-\frac{\alpha^2}{4}QS^{kl}\Big(\frac{\partial V}{\partial x^k}\Big)\Big(\frac{\partial}{\partial x^l}+i\alpha A_l\Big)-\frac{\alpha^2}{4}Qg^{kl}\Big(\frac{\partial V}{\partial x^k}\Big)\Big(\frac{\partial}{\partial x^l}+i\alpha A_l\Big)\\&-(E-V)-\tfrac{1}{2}\alpha^2(E-V)^2+U\Big]\Phi_1=0\end{aligned}\tag{25}$$

where

$$\begin{aligned}U=&-\frac{i}{2}g^{kl}\Big(\Gamma'_k\frac{\partial}{\partial x^l}+\Gamma'_l\frac{\partial}{\partial x^k}\Big)+\tfrac{1}{2}g^{kl}\Gamma'_k\Gamma'_l-\tfrac{1}{16}S^{kl}S_{mn}R^{mn}{}_{kl}\\&-\frac{i}{2}\frac{1}{\sqrt{g}}\frac{\partial}{\partial x^k}(\sqrt{g}g^{kl}\Gamma'_l)+\tfrac{1}{2}\alpha g^{kl}(\Gamma'_kA_l+\Gamma'_lA_k)\\&-\frac{i}{4}\alpha^2QS^{kl}\Big(\frac{\partial V}{\partial x^k}\Big)\Gamma'_l-\frac{i}{4}\alpha^2Qg^{kl}\Big(\frac{\partial V}{\partial x^k}\Big)\Gamma'_l.\end{aligned}\tag{26}$$

This equation (25) can be compared with the traditional 'flat' Pauli equation (Slater 1968)

$$\begin{aligned}\{&\tfrac{1}{2}(\boldsymbol{p}-\alpha\boldsymbol{A})^2-\tfrac{1}{2}\alpha\boldsymbol{\sigma}\cdot\boldsymbol{H}+\tfrac{1}{4}i\alpha^2Q\boldsymbol{\sigma}\cdot[(\boldsymbol{p}V)\wedge(\boldsymbol{p}-\alpha\boldsymbol{A})]\\&+\tfrac{1}{4}\alpha^2Q(\boldsymbol{p}V)\cdot(\boldsymbol{p}-\alpha\boldsymbol{A})-(E-V)-\tfrac{1}{2}\alpha^2(E-V)^2\}\Phi_1=0.\end{aligned}\tag{27}$$

One easily recognises that the four first terms of (25) are the 'curved form' of the four first terms of the classical Pauli equation (27), while the remaining terms U of (25) are supplementary terms which vanish at the traditional flat limit.

For the case of a spherical three-space, the line element is the spatial part of (8),

$$ds_0^2=R^2\,d\chi^2+R^2\sin^2\chi(d\theta^2+\sin^2\theta\,d\phi^2),\tag{28}$$

and consequently

$$\begin{aligned}&\sqrt{g}=R^3\sin^2\chi\sin\theta,\\&\tilde{\sigma}^1=\frac{1}{R}\sigma_\chi,\qquad\tilde{\sigma}^2=\frac{1}{R\sin\chi}\sigma_\theta,\qquad\tilde{\sigma}^3=\frac{1}{R\sin\chi\sin\theta}\sigma_\phi,\\&\sigma_\chi=\sigma^1\sin\theta\cos\phi+\sigma^2\sin\theta\sin\phi+\sigma^3\cos\theta,\end{aligned}\tag{29}$$

$$\sigma_\theta = \sigma^1 \cos\theta \cos\phi + \sigma^2 \cos\theta \sin\phi - \sigma^3 \sin\theta,$$

$$\sigma_\phi = -\sigma^1 \sin\phi + \sigma^2 \cos\phi,$$

$$\Gamma'_1 = 0, \qquad \Gamma'_k = \frac{\mathrm{i}}{2} \frac{1-\cos\chi}{\sin\chi} \tilde{\sigma}_k \tilde{\sigma}^1 \qquad \text{for } k = 2, 3.$$

The expression of the Pauli equation in a spherical three-space follows directly from equations (25), (26), (28) and (29).

4. Fine structure in a spherical three-space

Since we are only concerned with fine structure interaction terms, we shall consider the Pauli equation in a spherical three-space for the particular case where $A_k = 0$ for $k = 1, 2, 3, A_0 = V$ is the 'curved' form of the Coulomb potential, and for $Q(x) = 1 - \frac{1}{2}\alpha^2(E - V)$. When going to the non-relativistic limit of the Pauli equation (25) as is usually done, i.e. when introducing the spin operator $\boldsymbol{s} = \frac{1}{2}\boldsymbol{\sigma}$, one obtains (in au) (see appendix 1)

$$\left(-\tfrac{1}{2}\Delta + V + \frac{1}{2}\frac{\alpha^2 Z}{R^3 \sin^3\chi}\boldsymbol{l}\cdot\boldsymbol{s} - \tfrac{1}{2}\alpha^2(E-V)^2 + \tfrac{1}{8}\alpha^2\Delta V + U - E\right)\psi = 0 \tag{30}$$

where

$\Delta = (R^2 \sin^2\chi)^{-1}[(\partial/\partial\chi)(\sin^2\chi\, \partial/\partial\chi) - \boldsymbol{l}^2]$ is the spherical three-space Laplacian,

$$V = -(Z/R)\cot\chi,$$

$$U = \frac{(1-\cos\chi)}{R^2 \sin^2\chi}\boldsymbol{l}\cdot\boldsymbol{s} + \frac{1}{4}\left(\frac{1-\cos\chi}{R\sin\chi}\right)^2 + \frac{3}{4R^2} + \frac{1}{4}\frac{Z\alpha^2(1-\cos\chi)}{R^3\sin^3\chi}.$$

One recognises in (30) the Schrödinger hydrogenic wave equation in a spherical three-space completed by the 'curved' form of the Landé spin–orbit interaction, by the terms $-\frac{1}{2}\alpha^2(E-V)^2$ and $\frac{1}{8}\alpha^2(\Delta V)$, which are equivalent to the relativistic and Darwin corrections, and by an additional term U which vanishes at the flat limit ($R \to \infty$). As is usually done, the contributions to the energy arising from these terms are calculated by perturbation. We use as a basis the curved hydrogenic wavefunctions $\psi_{nlm}(\chi, \theta, \phi)$. These functions are already known (Bessis and Bessis 1979):

$$\psi_{nlm} = (\sin\chi)^{-1}\mathcal{R}_{nl}(\chi)Y_l^m(\theta, \phi) \tag{31}$$

where

$$\mathcal{R}_{nl}(\chi) = \mathcal{N}_{nl}(\sin\chi)^n \exp(-ZR\chi/n)P_v^A(-\mathrm{i}\cot\chi),$$

n is the usual radial quantum number, Y_l^m are the spherical harmonics, $v = n - l - 1$ and $A = (-n - \mathrm{i}ZR/n, -n + \mathrm{i}ZR/n)$. In spite of the presence of the imaginary quantities, the Jacobi polynomial P_v^A in (31) is a real polynomial of $\cot\chi$; $\mathcal{N}_{nl}$ is a normalisation constant.

As already pointed out, our procedure of calculation of the energies differs from that of Tourrenc and Grossiord (1976) and Parker (1980). Indeed, our perturbation calculation is done in the basis of already 'curved' non-relativistic wavefunctions, while Tourrenc and Parker have used 'flat' unperturbed wavefunctions (non-relativistic and relativistic).

When gathering the different contributions to the total energy E, one gets

$$E = E_0 + E_1 + E_2$$

where

$$E_0 = -Z^2/2n^2 + (n^2-1)/2R^2, \tag{32}$$

$$E_1 = \tfrac{1}{4}Z\alpha^2[j(j+1) - l(l+1) - 3/4]\langle nl|(R^3 \sin^3\chi)^{-1}|nl\rangle$$
$$-\tfrac{1}{2}\alpha^2\langle nl|[E_0 + (Z/R)\cot\chi]^2 + \tfrac{1}{4}(Z/R)\Delta(\cot\chi)|nl\rangle, \tag{33}$$

$$E_2 = \tfrac{1}{2}[j(j+1) - l(l+1) + 1/4]\langle nl|(1-\cos\chi)/R^2 \sin^2\chi|nl\rangle + 1/2R^2$$
$$+\tfrac{1}{4}Z\alpha^2\langle nl|(1-\cos\chi)/R^3 \sin^3\chi|nl\rangle. \tag{34}$$

E_0 is just the exact eigenvalue of the 'curved' hydrogenic Schrödinger equation (Schrödinger 1940, Bessis and Bessis 1979) which, at the flat limit, reduces to the well known electrostatic hydrogenic energy. E_1 is the 'curved form' of the classical Landé term and of the relativistic correction and Darwin term. E_2 corresponds to additional 'curvature' contributions. This last expression has been rearranged after noting that $\frac{1}{4}[(1-\cos\chi)/R \sin\chi]^2 = -1/4R^2 + \frac{1}{2}(1-\cos\chi)/R^2 \sin^2\chi$.

In order to analyse the curvature effects on the fine structure theoretical spectra, one has to put in evidence the n and l dependence of the various integrals in (33) and (34). The expression of the second part of E_1 in terms of n and l can be obtained without any difficulty since, after a simple trigonometric transformation, it can be absorbed into the curved hydrogenic electrostatic Schrödinger equation. As in the flat space, the Darwin term only contributes when $l = 0$ (see appendix 2). The expressions of the remaining matrix elements are obtainable in principle, at least by brute termwise integration. In fact, the direct calculation leads to rather cumbersome expressions and, in the present paper, we shall consider only the particular cases $l = n-1$ and $l = n-2$. Then, the basic wavefunctions are respectively

$$\begin{aligned} \mathcal{R}_{nn-1} &= \mathcal{N}_{nn-1}(\sin\chi)^n \exp(-ZR\chi/n), \\ \mathcal{R}_{nn-2} &= \mathcal{N}_{n\,n-2}(\sin\chi)^n[(n-1)\cot\chi - ZR/n]\exp(-ZR\chi/n). \end{aligned} \tag{35}$$

Even in that case, the final expressions of matrix elements are lengthy and we have derived for them approximate expressions (see appendix 2).

Finally, one obtains

$$E = E_n + E_{nlj} \tag{36}$$

where

$$E_n = -Z^2/2n^2 + n^2/2R^2,$$

$$E_{nlj} = -\frac{Z^4\alpha^2}{2n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right) + \frac{1}{2R^2}[j(j+1) - l(l+1) + 1/4]K(n,l)$$
$$+\frac{Z^2\alpha^2}{2R^2}\left[[j(j+1) - l(l+1) - 3/4]L(n,l) + \left(\frac{n^2+1}{2n^2} - \frac{n}{l+1/2}\right) + \frac{1}{4n^2}\right].$$

For $l = n-1$ and $l = n-2$, the expressions of the $K(n,l)$ and the $L(n,l)$ parameters, in terms of the quantum number n, are given in table 1. All the curvature corrections

Table 1. Expressions of the fine structure parameters.

	$l=n-1$	$l=n-2$
$K(n,l)$	$1/2$	$\dfrac{8n^3-18n^2+9n-4}{4n(n-3/2)}$
$L(n,l)$	$\dfrac{6n^2-3n+1}{8n^2(n-1)(n-1/2)}$	$\dfrac{6n^3-9n^2+13n-6}{8n^2(n-2)(n-3/2)(n-1)}$

to the energy are at least of an order of magnitude of $1/R^2$ and, therefore, the associated shifts or splittings of the energy levels of the free atom would be detectable only in regions of large curvature. It should be noted first that the curvature contributions to the electronic energy E_n are positive and, in order that the electron remains bound to the point charge nucleus, the second term of E_n must not be as large as the first classical term. One gets the condition (in au) $R > n^2/Z$. The dependence of the fine structure energy E_{nlj} on the quantum numbers n, l and j being known, at least for $l=n-1$ and $l=n-2$, one could question about the order of magnitude of the radius of curvature R which allows the curvature corrections to the flat energies to be detectable. As a simple example, we have reported in table 2 the curvature contributions to the hydrogenic $n=2$ fine structure energy levels comparatively with the classical contributions. It is found that the inclusion of the curvature contributions leads to a shift of the non-degenerate $2p_{3/2}$ fine structure level and to a splitting Δ_c of the degenerate $2p_{1/2}$–$2s_{1/2}$ level. To be somewhat consistent, this modification of the theoretical spectra is compared, in table 2, with the non-relativistic† Lamb shift contributions $W_{nlj}=Z^4\alpha^2\mathcal{H}/n^3(l+1)(2l+1)$ for $j=l+1/2$ and $W_{nlj}=-Z^4\alpha^2\mathcal{H}/n^3l(2l+1)$ for $j=l-1/2$ where $\mathcal{H}=1.159\,644\,10^{-3}$ (Durand 1976). Obviously, the curvature induced splitting $\Delta_c \simeq 1/R^2$ of the $2p_{1/2}$–$2s_{1/2}$ level should be detectable only if R is extremely small: this splitting Δ_c would be comparable to the Lamb splitting for $R \simeq 2\times 10^{-3}$ cm (Parker 1980).

Table 2. Fine structure of the hydrogenic $n=2$ energy levels (in au).

	Electronic energy	Flat fine structure	Curvature fine structure contributions	Non-relativistic Lamb shift
$E_{2p_{3/2}}$		$-\dfrac{Z^4\alpha^2}{128}$	$\dfrac{1}{2R^2}-\dfrac{Z^2\alpha^2}{8R^2}$	$\dfrac{Z^4\alpha^2\mathcal{H}}{48}$
$E_{2p_{1/2}}$	$-\dfrac{Z^2}{8}+\dfrac{2}{R^2}$		$-\dfrac{1}{4R^2}-\dfrac{23Z^2\alpha^2}{32R^2}$	$-\dfrac{Z^4\alpha^2\mathcal{H}}{24}$
$E_{2s_{1/2}}$		$-\dfrac{5Z^4\alpha^2}{128}$	$\dfrac{3}{4R^2}-\dfrac{53Z^2\alpha^2}{32R^2}$	$\dfrac{Z^4\alpha^2\mathcal{H}}{8}$

† Although a non-relativistic calculation does not account satisfactorily for the observed Lamb splitting Δ_L of the $2p_{1/2}$–$2s_{1/2}$ level (these formulae $\Delta_L=67.7\,\mathrm{Mc\,s^{-1}}$; refined relativistic calculation $\Delta_L=1057.64(2)\,\mathrm{Mc\,s^{-1}}$ (Erickson and Yennie 1965); observed value $\Delta_L=1057.845(9)\,\mathrm{Mc\,s^{-1}}$ (Lundeen and Pipkin 1981).

5. Conclusion

Finally, we have obtained, via the non-relativistic limit of the Dirac–Pauli covariant equations, the spin-dependent one-electron terms of the Hamiltonian. This investigation has been performed within the framework of the simplistic model which has been proposed to investigate 'curvature effects' on the atomic spectra (see paper I). The 'curved form' of the classical Landé interaction and relativistic correction has been given and we have found some additional curvature induced terms which vanish at the classical flat limit. To our knowledge such expressions have not yet been given. Within a limited example we have put in evidence the curvature modifications to the flat fine structure energy levels: curvature induced shift on the non-degenerate levels and splitting of the degenerate ones. In this respect, these effects play a role analogous to the Lamb shift effects. Of course, these additional curvature contributions to the flat energies are ridiculously small when R is taken to be the universe mean radius of curvature ($R \simeq 10^{26}$ cm) (Steinmetz 1967). Nevertheless, as pointed out by Parker (1980), one can conceive the possible existence of cosmic regions of large curvature, for instance in the vicinity of microscopic black holes, in which curvature effects may be observable and then, owing to their specific dependence on the quantum numbers, distinguishable from the other perturbations of the energy levels. Let us recall that, when considering a space of constant negative curvature (open space), instead of a space of positive curvature (closed space), our procedure of calculation is formally analogous: one has to make the changes $\chi \to i\chi$, $R \to iR$ and $V(\chi) = -(Z/R)\cot\chi \to -(Z/R)(\coth\chi - 1)$.

The real usefulness and the physical implications of this non-relativistic simplistic model cannot be decided before investigating many other remaining points, such as the curved form of the hyperfine structure Hamiltonian, of the bielectronic fine structure terms (spin–other-orbit and spin–spin interactions), etc, which are needed to calculate the curvature effects on the theoretical fine and hyperfine spectra of many-electron atoms. A more trivial point, but not so plain, is also to obtain exact and general analytical expressions of the fine and hyperfine structure 'curved' parameters in terms of the quantum numbers. This last point is in progress and treated by the ladder operator techniques described in a previous paper (Bessis *et al* 1981). The development of other aspects of the model, particularly in quantum chemistry (parametric curvature, see paper I), is also under investigation†.

Appendix 1. Derivation of the fine structure terms in a spherical three-space

Since the S^{kl} spin tensor is antisymmetric and since, for the case of a spherical three-space, the Coulomb potential $V = -(Z/R)\cot\chi$ does not depend on θ and ϕ, the third term of the Pauli equation (25) reduces to

$$-\frac{\alpha^2}{4} S^{kl}\left(\frac{\partial V}{\partial x^k}\right)\frac{\partial}{\partial x^l} = -\frac{\alpha^2}{4}\left(\frac{dV}{d\chi}\right)\left(S^{12}\frac{\partial}{\partial\theta} + S^{13}\frac{\partial}{\partial\phi}\right)$$

$$= \frac{\alpha^2}{4}\frac{Z}{R^3\sin^3\chi}\left(-i\sigma_\phi\frac{\partial}{\partial\theta} + i\sigma_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right). \qquad \text{(A1.1)}$$

† Let us mention that Horak (1982) has obtained the $1/Z$ expansion of the $(1s)^2\,{}^1S$ energy for $Z = 0$ via the present curved model.

The last parenthesis is just the scalar product $2\boldsymbol{l}\cdot\boldsymbol{s}$ when written in polar coordinates. Therefore one gets the 'curved' form of the Landé spin–orbit term which has been given in (30).

In the same way as in the flat space, the fourth term of equation (25), i.e. the Darwin term, can be conveniently written

$$-\tfrac{1}{4}\alpha^2 g^{kl}(\partial V/\partial x^k)\partial/\partial x^l = \tfrac{1}{8}\alpha^2(\Delta V) - \tfrac{1}{8}\alpha^2[\Delta, V]. \tag{A1.2}$$

Finally, in the correct Hermitian non-relativistic limit of the Dirac equation (Baym 1969), only the term $\frac{1}{8}\alpha^2(\Delta V)$ will survive in (30). For a Coulomb potential, this term is essentially a contact interaction between the electron and the charge of the nucleus. Thus its contribution to the energy is zero except for 's' states ($l=0$): in that case it is the same as in the flat space, i.e. $-\alpha^2 Z^4/n^3$.

Since $\Gamma_1' = 0$, the first, second, fourth and sixth terms of U in equation (26) reduce to

$$\begin{aligned}
&-\frac{\mathrm{i}}{2} g^{kl}\left(\Gamma_k' \frac{\partial}{\partial x^l} + \Gamma_l' \frac{\partial}{\partial x^k}\right) \\
&\qquad = -\mathrm{i}\left(g^{22}\Gamma_2' \frac{\partial}{\partial\theta} + g^{33}\Gamma_3' \frac{\partial}{\partial\phi}\right) \\
&\qquad = \frac{1}{2}\left(\frac{1-\cos\chi}{R^2\sin^2\chi}\right)\left(-\mathrm{i}\sigma_\phi \frac{\partial}{\partial\theta} + \mathrm{i}\frac{\sigma_\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right)
\end{aligned} \tag{A1.3}$$

where, again, the last parenthesis is just the scalar product $2\boldsymbol{l}\cdot\boldsymbol{s}$,

$$\tfrac{1}{2} g^{kl}\Gamma_k'\Gamma_l' = \tfrac{1}{2}(g^{22}(\Gamma_2')^2 + g^{33}(\Gamma_3')^2) = \frac{1}{4}\left(\frac{1-\cos\chi}{R\sin\chi}\right)^2 I, \tag{A1.4}$$

$$\begin{aligned}
&-\frac{\mathrm{i}}{2}\frac{1}{\sqrt{g}}\left(\frac{\partial}{\partial x^k}\sqrt{g}\, g^{kl}\Gamma_l'\right) \\
&\qquad = -\frac{\mathrm{i}}{2}\frac{1}{\sqrt{g}}\left(\frac{\partial}{\partial\theta}(\sqrt{g}\, g^{22}\Gamma_2') + \frac{\partial}{\partial\phi}\sqrt{g}\, g^{33}\Gamma_3'\right) \\
&\qquad = -\frac{\mathrm{i}}{2R^3\sin^2\chi\sin\theta}\left(\frac{R}{2}(1-\cos\chi)\cos\theta\,\sigma_\phi - \frac{R}{2}(1-\cos\chi)\frac{\partial}{\partial\phi}\sigma_\theta\right),
\end{aligned} \tag{A1.5}$$

and this term is zero, since $(\cos\theta\,\sigma_\phi = (\partial/\partial\phi)\sigma_\theta)$

$$\begin{aligned}
&-\tfrac{1}{4}\alpha^2 S^{kl}(\partial V/\partial x^k)\Gamma_l' \\
&\qquad = -\tfrac{1}{4}\mathrm{i}\alpha^2(\mathrm{d}V/\mathrm{d}\chi)(S^{12}\Gamma_2' + S^{13}\Gamma_3') \\
&\qquad = -\frac{\mathrm{i}}{4}\alpha^2\frac{Z}{R}\frac{1}{\sin^2\chi}\frac{\mathrm{i}(1-\cos\chi)}{2\sin\chi}(\tilde\sigma^1\tilde\sigma^2\tilde\sigma_2\tilde\sigma^1 + \tilde\sigma^1\tilde\sigma^3\tilde\sigma_3\tilde\sigma^1).
\end{aligned} \tag{A1.6}$$

Since $\tilde\sigma^2\tilde\sigma_2 = \tilde\sigma^3\tilde\sigma_3 = I$ and $\tilde\sigma^1\tilde\sigma^1 = I/R^2$, one gets the final expression given in (30).

It can be shown by direct calculation that the fourth term of U in equation (26) can be alternatively written $\operatorname{div}\Gamma_k'$ and vanishes. The last term of U also vanishes since V depends only on χ and $\Gamma_1' = 0$.

Let us consider the third term of U and introduce the spin curvature tensor

$$R_{kl} = -\tfrac{1}{4}S_{mn}R^{mn}{}_{kl} \tag{A1.7}$$

which is defined by (see, for instance, Pagels 1965)

$$R_{kl} = -\left[\frac{\partial}{\partial x^k} + i\Gamma'_k, \frac{\partial}{\partial x^l} + i\Gamma'_l\right] = i\left(\frac{\partial \Gamma'_k}{\partial x^l} - \frac{\partial \Gamma'_l}{\delta x^k}\right) + [\Gamma'_k, \Gamma'_l]. \tag{A1.8}$$

For the case of a spherical three-space, the only non-vanishing components are

$$R_{12} = -R_{21} = -\tfrac{1}{2}i\tilde{\sigma}_\phi \sin\chi, \qquad R_{13} = -R_{31} = \tfrac{1}{2}i\tilde{\sigma}_\theta \sin\chi \sin\theta, \tag{A1.9}$$
$$R_{23} = -R_{32} = -\tfrac{1}{2}i\tilde{\sigma}_\chi \sin^2\chi \sin\theta.$$

Then, since $|\tilde{\sigma}_\phi|^2 = |\tilde{\sigma}_\theta|^2 = |\tilde{\sigma}_\chi|^2 = I$, the third term of U in equation (26) reduces to

$$-\tfrac{1}{16}S^{kl}S_{mn}R^{mn}{}_{kl} = 3/4R^2. \tag{A1.10}$$

Appendix 2. Relativistic kinetic correction and fine structure integrals

A2.1. n and l dependence of the relativistic correction

One notes that

$$\left(E + \frac{Z}{R}\cot\chi\right)^2 = E^2 - \frac{Z^2}{R^2} + \frac{Z^2}{R^2}\frac{1}{\sin^2\chi} + \frac{2ZE}{R}\cot\chi. \tag{A2.1}$$

Thus, after introducing this term into the curved hydrogenic Schrödinger equation and separating the variables, one is led to solve the following eigenequation:

$$[d^2/d\chi^2 - \gamma(\gamma+1)/\sin^2\chi + 2ZR(1+\alpha^2E)\cot\chi + \lambda]\mathscr{R}'(\chi) = 0 \tag{A2.2}$$

where

$$\gamma(\gamma+1) = l(l+1) - Z^2\alpha^2 \qquad \text{or} \qquad \gamma = -\tfrac{1}{2} + [(l+1/2)^2 - Z^2\alpha^2]^{1/2},$$
$$\lambda = 2R^2E + 1 + \alpha^2(R^2E^2 - Z^2).$$

As previously pointed out in I, the ladder operator method is particularly suitable for solving the eigenequation. Within the Infeld and Hull (1951) classification, this equation is a type E (class I) factorisable equation with eigenvalue

$$\lambda_v = (v+\gamma+1)^2 - Z^2R^2(1+\alpha^2E)^2/(v+\gamma+1)^2 \tag{A2.3}$$

where $v = n - l - 1$ is a non-negative integer. Consequently

$$E = -\frac{1}{\alpha^2} + \frac{1}{\alpha^2}\left(\frac{1+\alpha^2[(v+\gamma+1)^2 - 1 + Z^2\alpha^2]/R^2}{1 + Z^2\alpha^2/(v+\gamma+1)^2}\right)^{1/2}. \tag{A2.4}$$

Finally, when retaining in (A2.4) the terms up to α^2, one finds

$$E = -\frac{Z^2}{2n^2} + \frac{n^2-1}{2R^2} - \frac{Z^4\alpha^2}{2n^3}\left(\frac{1}{l+1/2} - \frac{3}{4n}\right) - \frac{Z^2\alpha^2}{4R^2}\left(\frac{n^2-1}{n^2} + \frac{2n-2l-1}{l+1/2}\right). \tag{A2.5}$$

A2.2. Calculation of the fine structure integrals

Owing to the expression (32) of the wavefunctions, the calculation of the fine structure parameters in (31), either directly or after one part integration, can be reduced to the

evaluation of the basic couple of integrals

$$I(q)=\int_0^{\pi} e^{-p\chi}(\sin\chi)^{2q}\,d\chi, \qquad J(q)=\int_0^{\pi} e^{-p\chi}(\sin\chi)^{2q-1}\,d\chi, \tag{A2.6}$$

where $p=2ZR/n$ and q is a positive integer. From tables, one gets (Gradshteyn and Ryzhik 1980)

$$\begin{aligned} I(q)&=[(2q)!(1-e^{-p\pi})]\Big/\Big(p^{2q+1}\prod_{u=1}^{q}(1+a_u)\Big),\\ J(q)&=[(2q-1)!(1+e^{-p\pi})]\Big/\Big(p^{2q}\prod_{u=1}^{q}(1+b_u)\Big), \end{aligned} \tag{A2.7}$$

where

$$a_u=(2u/p)^2, \qquad b_u=[(2u-1)/p]^2.$$

As can be inferred from (A2.7), all the integrals will involve the factors $F=(1\pm e^{-p\pi})/(1-e^{-p\pi})$ and $G=\prod_{u=1}^{s}(1+a_u)/\prod_{u=1}^{r}(1+b_u)$. In order to put in evidence the contributions due to the curvature, we have introduced two basic approximations. On one hand, since $p=2ZR/n$, the first factor F, which is either 1 or coth p, is always made equal to 1. On the other hand, since obviously $b_u \ll 1$, and owing to their expressions, the ratios of finite products G can be written

$$G\simeq\prod_{u=1}^{s}(1+a_u)\prod_{v=1}^{r}(1-b_v) \tag{A2.8}$$

or

$$G\simeq 1+\sum_{u=1}^{s}a_u-\sum_{v=1}^{r}b_v+\ldots.$$

Owing to the above expressions of a_u and b_u, one gets

$$G\simeq 1+\frac{4}{p^2}\sum_{u=1}^{s}u^2+\frac{1}{p^2}\sum_{v=1}^{r}(2v-1)^2+O\Big(\frac{1}{p^4}\Big). \tag{A2.9}$$

From tables (Gradshteyn and Ryzhik 1980)

$$\sum_{u=1}^{s}u^2=\frac{s(s+1)(2s+1)}{6}, \qquad \sum_{v=1}^{r}(2v-1)^2=\frac{r(4r^2-1)}{3}, \tag{A2.10}$$

and finally, one obtains

$$G=1+\frac{2s(s+1)(2s+1)-r(4r^2-1)}{3p^2}+O\Big(\frac{1}{p^4}\Big). \tag{A2.11}$$

Finally, one finds respectively for $l=n-1$ and $l=n-2$

$$\langle nl|(R^3\sin^3\chi)^{-1}|nl\rangle=\begin{cases}\xi_{nn-1}[1+n^2(6n^2-3n+1)/4Z^2R^2]\\ \xi_{nn-2}[1+(6n^4-9n^3+13n^2-6n)/4Z^2R^2]\end{cases} \tag{A2.12}$$

where ξ_{nl} is the flat limit of the Landé fine structure parameter,

$$\xi_{nl}=\langle nl|r^{-3}|nl\rangle=Z^3/n^3l(l+1/2)(l+1), \tag{A2.13}$$

$$\langle nl|\,1-\cos\chi/R^2\sin^2\chi\,|nl\rangle=\begin{cases}1/2R^2\\ \dfrac{1}{2R^2}\quad\dfrac{8n^3-18n^2+9n-4}{n(2n-3)}\end{cases}\tag{A2.14}$$

$$\langle nl|(1-\cos\chi)/R^3\sin^3\chi|nl\rangle=Z/2R^2n^2.\tag{A2.15}$$

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