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Abstract. The determination of atomic wavefunctions when the usual Euclidean flat space is substituted by a spherical 3-space is investigated. Introducing hyperspherical coordinates (χ, θ, φ) and the 'curved' form $(1/R) \cot \chi$ of the Coulomb potential, 'curved hydrogenic orbitals'—solutions of the non-relativistic wave equation—are obtained using the ladder operator technique. A multipolar expansion of the bi-electronic repulsion potential is given, allowing the computation of curvature-dependent bi-electronic repulsion integrals. Some interesting features of this 'curved model', which of course gives again the usual flat results (as the radius of curvature $R \to \infty$), are pointed out.

Firstly we have to say that the aim of this paper is not at all to dare to introduce† the extremely feeble curvature of the Universe, related to gravitational theories, into atomic calculations in order to take into account its additional energetic contributions. Nevertheless, it should not be very surprising that even the slightest modification of the structure of the physical space could modify the wavefunctions and spectrum significantly. For instance, as first pointed out by Schrödinger (1940), the consideration of curvature may present some interesting features, such as resolving the continuous hydrogenic spectrum into an intensely crowded line spectrum. Furthermore, from a computational point of view, the radius of curvature R can be considered merely as an additional parameter to be adjusted in a variational calculation, i.e. more physically, that would amount to compensating for the lack of electronic correlation by a local modification of the geometry. From a practical point of view one could also question whether the consideration of a curvature parameter could possibly be used as an expedient to find more easily the usual flat results at the limit $R \to \infty$. Finally it may be also advantageous to transform the radial variable r, with infinite range $[0, \infty]$, of the flat space into an angular variable χ, with finite range $[0, \pi]$. For all these reasons and others unformulated, it seems worthwhile to explore the tractability of the problem. Even though a relativistic approach, via the covariant Dirac equation, would be expected to be more consistent with curvature considerations, as a first step we shall essentially investigate, within a non-relativistic 'curved' model, the 'curved' form of the electrostatic Coulomb potential. Magnetic interactions, via the Dirac–Pauli covariant equations, will be considered elsewhere (Bessis *et al* 1978).

Let us substitute for the usual three-dimensional Euclidean flat space a 'curved space' with constant positive curvature, i.e. a three-dimensional hypersphere imbedded in a four-dimensional Euclidean space. This simple model of a closed universe ensures

† Except maybe when dealing with some cosmological effects (Davies 1976). This is really far from our purpose.

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spatial isotropy and homogeneity. Solutions of quantum mechanical problems in this curved space would be expected to converge towards solutions of the flat space problems in the limit as the radius R of the space increases to infinity. Extending the ordinary spherical scheme in a four-dimensional Euclidean space E_4, the Cartesian coordinates become

$$x^1 = R \sin\chi \sin\theta \cos\varphi, \qquad x^2 = R \sin\chi \sin\theta \sin\varphi,$$
$$x^3 = R \sin\chi \cos\theta, \qquad x^4 = R \cos\chi. \tag{1}$$

Now consider the three-dimensional subspace such that $\Sigma_i (x^i)^2 = R^2$, where R is a constant. When θ and φ lie within their traditional bounds $0 \leq \varphi \leq 2\pi$, $0 \leq \theta \leq \pi$, the surface of this hypersphere is scanned in just one way when $0 \leq \chi \leq \pi$. The line element of this spherical 3-space is

$$ds^2 = R^2[d\chi^2 + \sin^2\chi(d\theta^2 + \sin^2\theta\, d\varphi^2)]. \tag{2}$$

If we let $R \to \infty$, $\chi \to 0$ so that $\chi R = r$ remains finite, this line element reduces to that of Euclidean space, in which r, θ, φ are the usual polar coordinates. The infinitesimal area of the hypersphere is given by

$$d\tau = R^3 \sin^2\chi \sin\theta\, d\chi\, d\theta\, d\varphi. \tag{3}$$

The Laplacian operator is

$$\nabla^2 = \frac{1}{R^2 \sin^2\chi}\left[\frac{\partial}{\partial\chi}\left(\sin^2\chi \frac{\partial}{\partial\chi}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$
$$= \frac{1}{R^2\sin^2\chi}\left[\frac{\partial}{\partial\chi}\left(\sin^2\chi\frac{\partial}{\partial\chi}\right) - l^2\right], \tag{4}$$

where l is just the usual three-dimensional angular momentum vector operator.

We shall assume that a time-independent N-electron Schrödinger equation holds and has the form

$$\left(\sum_{i=1}^{N}(-\tfrac{1}{2}\nabla_i^2 + V_i) + \sum_{i<j} V_{ij}\right)\Psi = E_T\Psi, \tag{5}$$

where E_T is the energy in standard units. We have to specify the form of the electrostatic potentials V_i and V_{ij}. We demand that $V_i \to 1/r_i$ as $R \to \infty$, $\chi_i \to 0$ and $\chi_i R = r_i$, and that $V_{ij} \to 1/r_{ij}$.

The required Coulomb potential function V_{ij} must depend only on the interparticle distance and, moreover, has to be an harmonic function, i.e. the solution of the Laplace equation $\nabla_i^2 V_{ij} = \nabla_j^2 V_{ij} = 0$. The 'angular separation' ω_{ij} between two particles i and j located on the hyperspace imbedded in E_4 is defined by

$$\cos\omega_{ij} = \sum_{u=1}^{4} \frac{1}{R^2} x_i^u x_j^u. \tag{6}$$

From (1) we obtain

$$\cos\omega_{ij} = \cos\chi_i \cos\chi_j + \sin\chi_i \sin\chi_j \cos\gamma_{ij}, \tag{7}$$

with

$$\cos\gamma_{ij} = \cos\theta_i \cos\theta_j + \sin\theta_i \sin\theta_j \cos(\varphi_i - \varphi_j).$$

In particular the angular separation between a current point $P(\chi, \theta, \varphi)$ of the hypersphere and the origin $O(x^1 = x^2 = x^3 = 0, x^4 = R)$ is $\cos\omega = \cos\chi$ and, as expected, the Coulomb potential V_i is a function of the single variable χ_i. Hence, in order to obtain the interparticle potential V_{ij}, one has first to find the single-variable harmonic potential $V(\chi)$ and substitute ω_{ij} for χ. From (4), $V(\chi)$ is the solution of the Laplace equation

$$\frac{1}{R^2}\frac{\partial}{\partial\chi}\left(\sin^2\chi\frac{\partial}{\partial\chi}\right)V(\chi) = 0. \tag{8}$$

The required solution is (Schrödinger 1941, Teague and Thomas 1973)

$$V = (\cot\chi)/R, \tag{9}$$

and consequently

$$V_{ij} = (\cot\omega_{ij})/R. \tag{10}$$

Indeed, this solution is well behaved in the sense that for $R \to \infty$ it converges to the correct flat limit. Since the geodesic distance between particles i and j is $r_{ij} = R\omega_{ij}$ (Eisenhart 1926),

$$V_{ij} = \frac{1}{R}\cot\left(\frac{r_{ij}}{R}\right) = \frac{(1/R)\cos(r_{ij}/R)}{\sin(r_{ij}/R)} \underset{R\to\infty}{\longrightarrow} \frac{1}{r_{ij}}. \tag{11}$$

Let us now consider the determination of the 'curved' hydrogenic orbitals. The one-electron Schrödinger equation is

$$\left\{-\frac{1}{2R^2\sin^2\chi}\left[\frac{\partial}{\partial\chi}\left(\sin^2\chi\frac{\partial}{\partial\chi}\right) - l^2\right] - \frac{Z}{R}\cot\chi\right\}\phi = E\phi, \tag{12}$$

where Z is the charge of the nucleus which is assumed to be fixed at the origin. The separation of variables is obviously achieved by setting

$$\phi = \mathcal{S}(\chi)Y_l^m(\theta, \varphi) = (1/\sin\chi)U(\chi)Y_l^m(\theta, \varphi), \tag{13}$$

where the Y_l^m are the usual spherical harmonics. Thus $U(\chi)$ has to be a square integrable solution of the equation

$$\left(\frac{d^2}{d\chi^2} - \frac{l(l+1)}{\sin^2\chi} + 2ZR\cot\chi + \lambda\right)U(\chi) = 0, \tag{14}$$

with $\lambda = 2R^2E + 1$.

As pointed out by Schrödinger (1940), the ladder operator method is particularly suitable for solving the eigenequation (14). Within the Infeld and Hull (1951) classification, this equation is a type E (class I) factorisable equation. When introducing the usual radial quantum number n, with the associated quantification condition

$$n - l - 1 = v, \tag{15}$$

where v is a non-negative integer, one obtains the following expressions of the eigenvalues: $\lambda_n = n^2 - Z^2R^2/n^2$. Hence the energy levels are

$$E_n = -Z^2/2n^2 + (n^2 - 1)/2R^2. \tag{16}$$

This expression was first obtained by Schrödinger (1941), who put in evidence the unusual and interesting feature of the Kepler motion in the hypersphere. Indeed, there are now only discrete states, and the passing through zero of the energy levels is allowed by continuity as n increases. As pointed out from the beginning, the additional curvature contribution to the flat transition energies is ridiculously small when R is taken to be the Universe radius of curvature ($R \simeq 10^{26}$ cm) (Steinmetz 1967). Nevertheless, the discretisation of the spectrum due to the closure of the Universe may have advantages in atomic calculations.

Using previous results (Hadinger *et al* 1974), the eigenfunctions U_{nl} of (14) are obtained in closed form, i.e. the following expressions of the 'pseudo-radial' part $\mathcal{S}_{nl}(\chi)$ of the 'curved' hydrogenic orbitals:

$$\mathcal{S}_{nl}(\chi) = \mathcal{N}_{nl}(\sin\chi)^{n-1}\exp(-ZR\chi/n)P_v^A(-\mathrm{i}\cot\chi), \tag{17}$$

where

$$A = (-n - \mathrm{i}\,ZR/n, -n + \mathrm{i}\,ZR/n),$$

v is given by (15) and $\mathcal{N}_{nl}$ is the normalisation constant, such that

$$\mathcal{N}_{nl}^2 R^3 \int_0^\pi |\mathcal{S}_{nl}(\chi)|^2 \sin^2\chi\,\mathrm{d}\chi = 1. \tag{18}$$

In spite of the presence of the imaginary quantities, the Jacobi polynomial P_v^A in (17) is a real polynomial of $\cot\chi$. For instance, for $n = 3$ and $v = 1$,

$$\mathcal{S}_{3\mathrm{p}}(\chi) = \mathcal{N}_{3\mathrm{p}}\sin^2\chi\,\mathrm{e}^{-ZR\chi/3}(\cot\chi - ZR/6). \tag{19}$$

Since the orbitals (17) depend on R through the product ZR, one may conclude that there is equivalence between screening effects and a local curvature variation, i.e. within a variational calculation it is the same to vary the charge Z or the R parameter of the orbital.

Extension of the one-electron model to many-electron calculations can be done within the usual independent particle framework using determinant wavefunctions built on a basis of 'curved orbitals'. In the many-electron Schrödinger equation (5), the inter-electronic repulsion potential (corresponding to the flat limit $1/r_{ij}$) is now $(\cot\omega_{ij})/R$ (equation (10)). When calculating the many-electron energies and wavefunctions, the most difficult integrals to compute are the two-electron $(\cot\omega_{ij})/R$ integrals.

Using the Fourier expansion of $\cos\omega$ (Dwight 1934) one may write

$$\frac{1}{R}\cot\omega_{ij} = \frac{8}{\pi R}\sum_{k=1}^{\infty}\frac{k}{4k^2-1}\frac{\sin 2k\omega_{ij}}{\sin\omega_{ij}} \qquad (0 < \omega_{ij} < \pi, \text{ exclusive}). \tag{20}$$

Next, using the hyperspherical expansion of $\sin 2k\omega/\sin\omega$ (Fock 1935), one obtains the (χ_i, χ_j) symmetrical expression

$$\frac{1}{R}\cot\omega_{ij} = \frac{16}{R}\sum_{k=1}^{\infty}\frac{1}{4k^2-1}\sum_{l,m}\Pi_l(2k,\chi_i)\Pi_l(2k,\chi_j)Y_l^{m*}(\theta_i\varphi_i)Y_l^m(\theta_j\varphi_j), \tag{21}$$

where the $\Pi_l(2k, \chi)$ are the Fock functions related to the Gegenbauer polynomials. These $\Pi_l(2k, \chi)$ are solutions of a factorisable eigenequation (type A, class I) and easily obtainable in closed form.

The bi-electronic repulsive integral is readily integrated in θ and φ using '$3j$' symbols:

$$\langle\phi_1\phi_2\frac{1}{R}\cot\omega_{ij}\phi_3\phi_4\rangle=\frac{4}{\pi R}[(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)]^{1/2}$$
$$\times(-)^{m_2-m_3}\sum_l(2l+1)\begin{pmatrix}l_1 & l & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & l & l_2\\ -m_1 & m_1-m_2 & m_2\end{pmatrix}$$
$$\times\begin{pmatrix}l_3 & l & l_4\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_3 & l & l_4\\ -m_3 & m_3-m_4 & m_4\end{pmatrix}\langle 12\|34\rangle_l, \tag{22}$$

where

$$\langle 12\|34\rangle_l=\sum_{k=1}^{\infty}\frac{1}{4k^2-1}I_{kl}(1,2)I_{kl}(3,4), \tag{23}$$

$$I_{kl}(s,t)=\mathcal{N}_s\mathcal{N}_tR^3\int_0^{\pi}\mathcal{S}_s(\chi)\Pi_l(2k,\chi)\mathcal{S}_t(\chi)\sin^2\chi\,\mathrm{d}\chi. \tag{24}$$

In (22) the range and parity of l are, as usual, restricted by the non-vanishing conditions of the $3j$ symbols. The integrals I_{kl} can be calculated in closed form. One interesting consequence of expansion (22) is that the bi-electronic radial integral (in χ)$\langle\|\rangle_l$ is factorised, but on the other side one has to sum an infinite series which is rather tedious to perform. This symmetrical expansion has to be compared with the flat limit

$$\frac{1}{r_{ij}}=8\sum_{l=0}^{\infty}\sum_{m=-l}^{l}Y_l^{m*}(\theta_i\varphi_i)Y_l^m(\theta_j\varphi_j)\int_0^{\infty}j_l(r_ik)j_l(r_jk)\,\mathrm{d}k, \tag{25}$$

where the $j_l(x)$ are the spherical Bessel functions.

An alternative expansion of $(\cot\omega_{ij})/R$ can be obtained. For this purpose it is more convenient to define the $\Pi_l(2k,\chi)$ functions by their Rodrigues formula

$$\Pi_l(2k,\chi)=\frac{2k(\sin\chi)^l}{4k^2(4k^2-1)\ldots(4k^2-l^2)}\left(\frac{\mathrm{d}}{\mathrm{d}(\cos\chi)}\right)^l\frac{\sin 2k\chi}{\sin\chi}. \tag{26}$$

One can write

$$\sum_{k=1}^{\infty}\frac{1}{4k^2-1}\Pi_l(2k,\chi_i)\Pi_l(2k,\chi_j)$$
$$=\left(\frac{1}{2}\right)^{2l+3}(\sin\chi_i)^l(\sin\chi_j)^l\left(\frac{\mathrm{d}}{\mathrm{d}u_i}\right)^l\left(\frac{\mathrm{d}}{\mathrm{d}u_j}\right)^l\frac{M_l(\chi_i-\chi_j)-M_l(\chi_i+\chi_j)}{\sin\chi_i\sin\chi_j}, \tag{27}$$

where

$$M_l(x)=\sum_{k=1}^{\infty}\frac{k^2\cos kx}{(k^2-1/4)k^2(k^2-1/4)\ldots(k^2-l^2/4)}. \tag{28}$$

Starting from M_0, which can be found elsewhere (Gradshteyn and Ryzhik 1965), these series can be calculated recursively when $0\leqslant x\leqslant\pi$, i.e. when

$$0\leqslant\chi_i\pm\chi_j\leqslant\pi. \tag{29}$$

After some manipulations, one obtains the required expansion of $(\cot\omega_{ij})/R$ in terms of χ_i and χ_j subject to condition (29) involving $\chi_i\geqslant\chi_j$. When introducing the traditional notation $\chi_>$ and $\chi_<$, this expansion becomes

$$\frac{1}{R}\cot\omega_{ij}=\frac{1}{R}\cot\chi_>+\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}Y_l^{m*}(\theta_i\varphi_i)Y_l^m(\theta_j\varphi_j)F_l(\chi_>)G_l(\chi_<), \tag{30}$$

with

$$F_l(\chi)=\frac{1}{(2l-1)!!}(\sin\chi)^l\left(\frac{\mathrm{d}}{\mathrm{d}(\cos\chi)}\right)^l\cot\chi,$$

$$G_l(\chi)=\frac{(-)^{l+1}(2l+1)!!}{(l-1)!(l+1)!}(\sin\chi)^l\left(\frac{\mathrm{d}}{\mathrm{d}(\cos\chi)}\right)^l\chi\cot\chi. \tag{31}$$

The expansion (30) of $(\cot\omega_{ij})/R$ in terms of the harmonic solutions $F_lY_l^m$ and $G_lY_l^m$ is the 'curved' homologue of the Laplace expansion

$$\frac{1}{r_{ij}}=\frac{1}{r_>}+\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{(2l+1)}Y_l^{m*}(\theta_i\varphi_i)Y_l^m(\theta_j\varphi_j)\frac{r_<^l}{r_>^{l+1}}. \tag{32}$$

It can be easily verified that, as expected, when $R\to 0$, $\chi\to 0$ and $\chi R=r$, the $F_l(\chi)$ and $G_l(\chi)$ functions converge to the flat radial harmonic functions $(1/r)^{l+1}$ and r^l respectively.

$F_l(\chi)$ is a polynomial of degree $(l+1)$ in $\cot\chi$, while $G_l=(-)^{l+1}[(2l+1)!!(2l-1)!!/(l+1)!(l-1)!]\chi F_l+g_l(\chi)$, where $g_l(\chi)$ is also a polynomial of degree l in $\cot\chi$ and of parity l. In particular, the dipolar ($l=1$) and quadrupolar ($l=2$) terms can be written

$$F_1(\chi)=1/\sin^2\chi,\qquad G_1(\chi)=\tfrac{3}{2}(\chi/\sin^2\chi-\cot\chi), \tag{33}$$
$$F_2(\chi)=\cot\chi/\sin^2\chi,\qquad G_2(\chi)=\tfrac{5}{2}(3\chi\cot\chi/\sin^2\chi+1-3/\sin^2\chi).$$

It seems to us that the expansion (31) is more suitable than (21) for computing the integrals. Indeed, the $\langle(\cot\omega_{ij})/R\rangle$ integral can be finally reduced to the calculation of elementary integrals $\int\exp(-2ZR\chi/n)\,(\sin\chi)^p(\cos\chi)^q\,\mathrm{d}\chi$ with p and q non-negative integers and with two types of intregration bounds $[0,\chi]$ and $[\chi,\pi/2]$. As an illustrative example, one finds

$$\left\langle 1\mathrm{s}\,1\mathrm{s}\,\frac{1}{R}\cot\omega_{ij}\,1\mathrm{s}\,1\mathrm{s}\right\rangle=\frac{1}{R}\left(\frac{ZR(5Z^2R^2+1)\coth ZR\pi}{2(4Z^2R^2+1)}+\frac{\pi Z^2R^2(Z^2R^2+1)}{2\sinh^2 ZR\pi}\right). \tag{34}$$

When $R\to\infty$, it can be checked that the first term of (34) converges toward the expected flat limit $\frac{5}{8}Z$, while the second term vanishes.

Anticipating further results concerning the fine structure terms of the Hamiltonian (Bessis *et al*), it should be interesting to note that within the 'curved' model the quadrupolar parameter $\langle F_2\rangle=\langle\cot\chi/\sin^2\chi\rangle$ and the Landé parameter $\langle 1/\sin^3\chi\rangle$ have different expressions, although their flat limit $\langle r^{-3}\rangle$ is the same. This result is to be compared in some way with the differentiation between dipolar magnetic and quadrupolar electric hyperfine $\langle r^{-3}\rangle$ parameters in the Dirac model (see e.g. Armstrong 1971).

Let us finally mention that when one considers a space of constant negative curvature (open space) instead of a space of positive curvature (closed space) the problem is also tractable. Briefly stated, one has to make the following changes: $\chi\to\mathrm{i}\,\chi$,

$R \to \mathrm{i}\,R$, $V(\chi) = (\cot\chi)/R \to (\coth\chi - 1)/R$. But, as has been shown by Infeld and Schild (1945), the hydrogenic spectrum exhibits a finite number of discrete energy levels in addition to a continuous spectrum. In this last case, the determination of electronic wavefunctions has not been considered.

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