

RAYLEIGH-RITZ METHODS FOR DIRAC HAMILTONIANS

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Abstract. *The absence of a finite lower bound on the spectrum of the Dirac Hamiltonian for hydrogenic atoms has been taken to imply that variational methods cannot be applied to this problem or, by extension, to any relativistic electronic structure calculation for many-electron systems based on Dirac theory. We show that this view is mistaken, and thereby validate retrospectively the large number of Dirac-Hartree-Fock(-Breit) self-consistent field calculations made over the last 40 years. L-spinors (pairs of two-component basis functions that generalize the well-known Coulomb Sturmians) provide countable complete bases which enable us to study convergence of Rayleigh-Ritz approximations for the Dirac hydrogen-like eigenvalue spectrum and (four-component) eigenspinors and of other observable quantities derived from them. Implications for the relativistic calculation of the electronic structure of atoms, molecules and condensed matter will be discussed.*

1 INTRODUCTION

We shall be concerned in this paper with the solution of quantum mechanical problems involving the Dirac operator in atomic and molecular physics, for which there is a voluminous literature [1, 2]. There are many textbooks on the Dirac operator both from mathematical and physical points of view [3]. The Dirac equation describes the quantum mechanics of fermions, in particular electrons and positrons, and its characteristics are woven into the theory of quantum electrodynamics and other quantum field theories [5]. The cited texts are aimed primarily at applications in particle physics. However, it is well-known that the electronic structure and properties of atoms, molecules and condensed matter show evidence of relativistic effects, particularly where heavy elements are concerned, as the bibliography published in book form by Pyykkö [2] with an aggregate of nearly 10,000 references attests! The field has continued to grow rapidly.

Unfortunately, there remains much confusion over the computational tools available for treating such many-electron systems. Although several standard relativistic atomic structure codes using Dirac theory itself are available (such as [6], for example), the majority of calculations for molecules or solids are based on semi-relativistic approximations whose errors are almost impossible to quantify. The main reason for this state of affairs can be seen by looking at the spectrum of the Dirac operator for a hydrogen-like atom, which consists of the intervals $(-\infty, -mc^2) \cup (mc^2, \infty)$ (where m is the electron rest mass and c the speed of light) together with an infinite point spectrum in the gap $(-mc^2, mc^2)$ with a limit point at mc^2 . Electronic structure calculations for many-electron systems often begin with the solution of self-consistent field equations, which are generally derived from a variational principle [7, 8]. In non-relativistic quantum theory, the spectrum is known to have a finite lower bound, and it is therefore assumed that the absence of a finite lower bound for the equivalent problem in Dirac theory rules out such methods. Although Dirac-Fock self-consistent field equations can be derived variationally and have been solved with great success by finite difference methods for many years [1, 9, 10], such assumptions raise doubts as to whether the results are really reliable. One purpose of this paper is to demonstrate the legitimacy of variational methods for Dirac one-electron and many-electron problems, providing a secure foundation for Dirac-Hartree-Fock-Breit self-consistent field calculations in atoms and molecules and for more accurate calculations of electron correlation effects using many-body theories.

The L-spinors were defined in [11] (see also [1, §22.6.3]). Because of their linear independence and completeness properties it is possible to study the convergence of the Rayleigh-Ritz method for the Dirac hydrogenic atom, of the eigenvalues and eigenvectors that it generates as well as of other properties that can be derived from them. L-spinors are unfortunately totally unsuitable for calculating the properties of many-electron systems, but other basis sets are available for that purpose.

2 THE RAYLEIGH-RITZ METHOD FOR SCHRÖDINGER AND DIRAC OPERATORS

Applications of the Rayleigh-Ritz method in nonrelativistic quantum mechanics usually assume a *self-adjoint, non-negative, compact* operator, T , defined on a domain \mathcal{D} , a subset of a Hilbert space \mathcal{H} . Such an operator has an ordered set of non-negative eigenvalues

$$0 \leq \lambda_1 \leq \lambda_2 \leq \dots$$

with due regard for multiplicity, with corresponding eigenfunctions ψ_1, ψ_2, \dots respectively. The *Rayleigh quotient*, defined (in Dirac bra-ket notation) by

$$R[\psi] := \langle \psi | T | \psi \rangle / \langle \psi | \psi \rangle, \quad (1)$$

evidently exists for all non-trivial $\psi \in \mathcal{D}$. We try to approximate ψ by its projection, $P_n \psi$, on a finite dimensional subspace $\mathcal{W}_n := \{\chi_1, \chi_2, \dots, \chi_n\} \subset \mathcal{D}$, so that

$$P_n \psi = c_1^n \chi_1 + c_2^n \chi_2 + \dots + c_n^n \chi_n, \quad (2)$$

where the coefficients c_i^n are in general complex. Thus $R[P_n \psi]$ reduces to the algebraic expression

$$F^n[\mathbf{c}^n] = \mathbf{c}^{n\dagger} \mathbf{T}^n \mathbf{c}^n / \mathbf{c}^{n\dagger} \mathbf{S}^n \mathbf{c}^n, \quad (3)$$

where $\mathbf{c}^n = (c_1^n, c_2^n, \dots, c_n^n)^t$, $\mathbf{c}^{n\dagger}$ is its Hermitian conjugate, and $\mathbf{T}^n, \mathbf{S}^n$ are $n \times n$ Hermitian matrices with elements

$$T_{ij}^n = \langle \chi_i | T | \chi_j \rangle, \quad S_{ij}^n = \langle \chi_i | \chi_j \rangle, \quad 1 \leq i, j \leq n \quad (4)$$

respectively. The Gram matrix \mathbf{S}^n must be positive definite if (3) is to have a meaning, so that the set \mathcal{W}_n must be linearly independent. The Gram matrix of such a linearly independent set reduces to the n -dimensional identity matrix if the functions χ_i are assumed orthonormal, but it is advisable not to restrict our choice of basis functions in this way.

Elementary calculus tells us how to find the stationary points of $F^n[\mathbf{c}^n]$ as the roots of the Galerkin equation [12, p. 395]

$$\mathbf{T}^n \mathbf{c}^n = \Lambda^n \mathbf{S}^n \mathbf{c}^n, \quad (5)$$

where Λ^n is a diagonal eigenvalue matrix whose elements can be ordered so that

$$0 < \Lambda_1^n \leq \Lambda_2^n \leq \dots \leq \Lambda_n^n,$$

with due regard for multiplicity. We denote the corresponding eigenvectors, the columns of \mathbf{c}^n , by $\mathbf{c}_1^n, \mathbf{c}_2^n, \dots, \mathbf{c}_n^n$.

It is customary in the quantum mechanical literature to show at this point that the lowest eigenvalue Λ_1^n is an upper bound to the true eigenvalue λ_1^n . This is attributed to the fact that T is a positive definite operator, and the conclusion is easily generalized to encompass all operators T which are bounded below. However, this needs to be seen in a more general setting given by the following theorem

Theorem 1 (Poincaré) [12, pp. 397–8]¹ *When T is a self-adjoint, non-negative, compact operator, the eigenvalues of the Galerkin equation are upper bounds to the target eigenvalues*

$$0 < \lambda_1 \leq \Lambda_1^n \leq \dots \leq \lambda_n \leq \Lambda_n^n.$$

Increasing the size of the set \mathcal{W}_n generally improves the approximation. In practice, one would like to use a complete set of functions $\mathcal{W} := \{\chi_i\}_{i=1}^\infty$ spanning the domain \mathcal{D} , so that \mathcal{W}_n spans an increasing subspace of \mathcal{D} as n increases. Then $\Lambda_i^n \rightarrow \lambda_i$ as $n \rightarrow \infty$ because the compact operator $P_n T \rightarrow T$ in the operator norm [12].

This theorem applies directly to the Schrödinger equation for the hydrogen-like atom. In conjunction with what is usually referred to in the literature as the Hylleraas-Undheim-Macdonald theorem [13], which states that the eigenvalues of the problem in \mathcal{W}_n separate those of \mathcal{W}_{n+1} :

$$0 < \Lambda_1^{n+1} \leq \Lambda_1^n \leq \dots \leq \Lambda_n^{n+1} \leq \Lambda_n^n \leq \Lambda_{n+1}^{n+1},$$

we infer that the sequence $\{\Lambda_n^n, \Lambda_n^{n+1}, \Lambda_n^{n+2} \dots\}$ decreases monotonically and, since it is bounded below, it has a limit point which is not less than λ_n . Conditions under which such sequences converge to the required limit λ_n were studied by Klahn and Bingel [14] who concluded it was sufficient that basis sets (of radial wave functions) must be complete in the Sobolev space $W_2^{(1)} \subset L^2$ consisting of functions in L^2 whose generalized first derivatives are also in L^2 . The norm in $W_2^{(1)}$ is defined by

$$\|\psi\|_{W_2^{(1)}}^2 = \|(1 + p^2)^{1/2}\psi\|_{L^2}^2. \quad (6)$$

where $\mathbf{p} = -i\nabla$ is the quantum mechanical momentum operator. This condition also suffices to establish convergence of $P_n\psi$ to ψ as $n \rightarrow \infty$. The analysis was subsequently extended [14] to include expectation value and transition matrix elements formed from the Rayleigh-Ritz eigenvectors.

3 THE DIRAC HAMILTONIAN FOR A HYDROGENIC ATOM

The Dirac Hamiltonian for a hydrogen-like system with a fixed point nucleus of charge Ze , where e is the proton charge, and Z is the atomic number is

$$H(Z) := H_0 - Z/r \quad (7)$$

using Hartree atomic units ($\hbar = 1$, $m = 1$, $e^2/4\pi\epsilon_0 = 1$), r is the electron-nuclear distance and

$$H_0 := c\boldsymbol{\alpha} \cdot \mathbf{p} + c^2\beta. \quad (8)$$

$\boldsymbol{\alpha}, \beta$ are the usual 4×4 Dirac matrices, $c \approx 137$ is the speed of light in Hartree units, and \mathbf{p} is the 3-momentum operator. We shall express the Dirac matrices in terms of the

¹Stakgold's inequalities [12] are reversed as he lists the eigenvalues in reverse order.

2×2 Pauli matrices $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ and the identity matrix \mathbf{I} :

$$\boldsymbol{\alpha} = \begin{bmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{bmatrix}, \quad \boldsymbol{\beta} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{bmatrix},$$

H_0 is essentially self-adjoint on $C_0^\infty(\mathbf{R}^3 \setminus 0)^4$ and self-adjoint on the Sobolev space $\mathcal{D}(H_0) = W_1(\mathbf{R}^3)^4 \subset L^2(\mathbf{R}^3)^4$ [4, Theorem 1.1]. Establishing a domain for $H(Z)$ seems more troublesome. Following the textbooks [15, 4], one tries to determine numbers b and $0 \leq a < 1$, such that $\|V\psi\| \leq a\|H_0\psi\| + b\|\psi\|$, from which one infers the domain on which $H(Z)$ is essentially self-adjoint using the Kato-Rellich Theorem [15, 4]. Such arguments give the disappointing result that $H(Z)$ is well-defined and essentially self-adjoint on $C_0^\infty(\mathbf{R}^3 \setminus 0)^4$ and self-adjoint on $\mathcal{D}(H_0)$ *only* if $Z/c < \sqrt{3}/2$ [4, Theorem 4.4]. Since $c \approx 137$ in atomic units, this restricts the potentials to $Z < 118$, which satisfactorily covers all elements in the Periodic Table. However, the standard textbook analytic solutions are well behaved for $Z \leq c^{-1} \approx 137$ and it would be nice to be able to extend the domain of self-adjointness when $118 < Z \leq 137$. Clearly we need to be a bit more subtle to obtain such a result.

There are two analytic solutions of the Dirac Coulomb problem: one is *regular* at $r = 0$ having amplitudes of order $O(r^\gamma)$ there (recall $\gamma = +\sqrt{\kappa^2 - Z^2/c^2}$), the other *irregular* and of order $O(r^{-\gamma})$. When $\kappa = \pm 1$ then $\gamma = 1/2$ at $Z/c = \sqrt{3}/2$. So for $Z < 118$, only the regular solution is square integrable near $r = 0$, whereas both solutions are square integrable for $Z > 118$, and a general square integrable eigensolution of the Dirac Coulomb problem is an arbitrary linear combination of the two. Order can be restored by noting that any solution containing a multiple of the irregular solution makes $\langle \psi | V | \psi \rangle$ infinite [1, §22.5], so that the physics requires exclusion of the irregular solution to make the expectation of V finite. This behaviour can also be interpreted in the language of the theory of differential equations either as a transition of the behaviour at the origin from a limit-point description for $\gamma > 1/2$ to a limit-circle description for $\gamma < 1/2$ [16, Chapter 11], or in terms of the theory of deficiency indices [15].

The idealized point charge nucleus is not a good enough model for the heavier elements, or for very accurate work anywhere in the Periodic Table, and one can then replace the Coulomb potential by one which is infinitely differentiable. In this case H is again essentially self-adjoint on $\mathcal{D}(H_0)$ [4, Theorem 4.3].

The extension to many-electron atoms or molecules is not considered in [4], but there seem to be no insuperable difficulties once the single particle case has been understood.

4 RAYLEIGH-RITZ METHOD FOR THE DIRAC OPERATOR

Consider the Dirac Coulomb atomic Hamiltonian

$$H(z) := c \boldsymbol{\alpha} \cdot \mathbf{p} + mc^2 \boldsymbol{\beta} - z/r \tag{9}$$

with $0 \leq z \leq Z$ on $\mathcal{D}(H_0) = W_1(\mathbf{R}^3)^4$. Equation (9) defines a family of Dirac Hamiltonians interpolating smoothly between $H(0) = H_0$ and $H(Z)$ where the Coulomb field

reaches its full strength.

Trial wavefunctions will be of the general form

$$\phi := \begin{bmatrix} \sum_{n=1}^N c_n^L M[L, n\kappa m, \mathbf{r}] \\ i \sum_{n=1}^N c_n^S M[S, n\kappa m, \mathbf{r}] \end{bmatrix}. \quad (10)$$

At this point, we assume only that the *two-component* expansion functions $M[T, n\kappa m, \mathbf{r}]$, $T = L, S$ are both complete in the appropriate two-dimensional function space; we shall discuss their form later. The Galerkin equations take the form

$$\begin{bmatrix} c^2 \mathbf{S}^{LL} + \mathbf{V}^{LL} & c \mathbf{\Pi}^{LS} \\ c \mathbf{\Pi}^{SL} & -c^2 \mathbf{S}^{SS} + \mathbf{V}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} = E \begin{bmatrix} \mathbf{S}^{LL} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} \quad (11)$$

in which all the submatrices are of dimension $N \times N$. The Gram matrices are denoted by \mathbf{S}^{TT} , $T = L, S$, and \mathbf{V}^{TT} are the corresponding matrices of the potential V . The matrices $\mathbf{\Pi}^{T\bar{T}}$ (where $\bar{T} = S$ when $T = L$ and *vice versa*) are given by

$$\begin{aligned} \mathbf{\Pi}_{nn'}^{LS} &:= \int M^\dagger[L, n\kappa m, \mathbf{r}] \boldsymbol{\sigma} \cdot \mathbf{p} M[S, n'\kappa m, \mathbf{r}] d\mathbf{r}, \\ \mathbf{\Pi}_{nn'}^{SL} &:= \int M^\dagger[S, n\kappa m, \mathbf{r}] \boldsymbol{\sigma} \cdot \mathbf{p} M[L, n'\kappa m, \mathbf{r}] d\mathbf{r}. \end{aligned}$$

The system is Hermitian and has real eigenvalues.

The operator $H(0)$ has a pure absolutely continuous spectrum consisting of two disjoint intervals $\sigma_- = (-\infty, -mc^2]$ and $\sigma_+ = [mc^2, \infty)$. Suppose that ϕ is an arbitrary trial function in $\mathcal{D}(H_0)$, and let

$$E_\phi(z) = \langle \phi | H(z) | \phi \rangle = E_\phi(0) - zv_{phi}$$

where $v_\phi = \langle \phi | 1/r | \phi \rangle > 0$. Suppose first that ϕ has been chosen so that $E_\phi(0) > mc^2$. Since $E_\phi(z)$ is a monotonically decreasing function² of z , we have

$$E_\phi(0) \geq E_\phi(z) \geq E_\phi(Z) > mc^2 + V_{min} \quad (12)$$

where

$$V_{min} = \inf_{\phi} \langle \phi | -Z/r | \phi \rangle.$$

Thus a sufficient condition for $E_\phi(Z)$ to lie in the bound state gap $(-mc^2, mc^2)$ is that $V_{min} > -2mc^2$. It follows that $H(Z) - V_{min}$ is a non-negative operator, and therefore has a lower bound on $\mathcal{D}_+(H_0) = \{\phi \in \mathcal{D}(H_0) : E_\phi(0) > mc^2\}$.

In the same manner, we see that when ϕ is in $\mathcal{D}_-(H_0) = \{\phi \in \mathcal{D}(H_0) : E_\phi(0) < -mc^2\}$, $E_\phi(Z) < -mc^2$. The two families of trial functions are clearly disjoint as long as $V_{min} >$

²For examples of this behaviour see [3, Greiner, Figs. 9.11 and 9.13].

$-2mc^2$. If Z is so large that $V_{min} < -2mc^2$, we expect one or more eigenfunctions to fall below $-mc^2$. For a discussion of possible consequences, see the book by Greiner [3].

This analysis applies also to the eigensolutions of the Galerkin equations (11) provided the spinor trial functions are properly defined (see below).

The inference is that as far as bound states and the positive continuum of the Dirac Hamiltonian for hydrogenic atoms are concerned, the convergence behaviour of Rayleigh-Ritz eigenvalues, eigenspinors and matrix elements should be very similar to the convergence behaviour of the corresponding Schrödinger eigenvalues, eigenfunctions and matrix elements as the basis set is enlarged. We should not expect to find any convergent sequences of eigenvalues with energies below $-mc^2$. This does not mean that the negative energy states are useless. In quantum electrodynamics (QED), the negative spectrum is reinterpreted as a continuum of positron scattering states. States in both continua are required for completeness on $\mathcal{D}(H_0)$, and play an important role in perturbation calculation of physical effects.

5 THE COULOMB STURMIAN FUNCTIONS

The nonrelativistic Sturmian functions are defined by [17] as the normalised solutions of the differential equation

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - 2E_0 + 2\alpha_{nl}V(r) \right] S_{nl}(r) = 0, \quad 0 < r < \infty, \quad (13)$$

vanishing at the endpoints $r = 0$ and $r = \infty$. The integers $n = 1, 2, 3, \dots$ and $l = 0, 1, \dots, n-1$ correspond to the usual nonrelativistic quantum numbers and E_0 is a fixed, negative number. The parameter α_{nl} must be adjusted to ensure that the boundary conditions are satisfied. The functions are orthonormal with respect to the weight function $V(r)$ (which must be strictly of one sign, usually negative) so that

$$\int_0^\infty S_{nl}(r)S_{n'l}(r)V(r)dr = -\delta_{nn'}. \quad (14)$$

The most important case is that in which $V(r)$ is a Coulomb potential

$$V(r) = -\frac{Z}{r}, \quad 0 < r < \infty.$$

We set $E_0 = -\lambda^2/2$, and rewrite (13) in terms of the independent variable $x = 2\lambda r$, so that

$$\left[-\frac{d^2}{dx^2} + \frac{l(l+1)}{x^2} + \frac{1}{4} - \frac{\alpha_{nl}Z}{\lambda x} \right] S_{nl}(x) = 0, \quad (15)$$

having the solutions

$$S_{nl}(x) := \mathcal{N}_{nl} s_{nl}(x), \quad s_{nl}(x) = e^{-x/2} x^{l+1} L_{n-l-1}^{2l+1}(x), \quad n = l+1, l+2, \dots, \quad (16)$$

which vanish at $x = 0$ and $x = \infty$ provided

$$n = \alpha_{nl}Z/\lambda.$$

The $L_k^\alpha(x)$ are Laguerre polynomials [18], and \mathcal{N}_{nl} is a normalization constant. When $\alpha \geq 1$ they are orthogonal on $(0, \infty)$ with weight function $w(x) = e^{-x}x^\alpha$, such that

$$\int_0^\infty e^{-x}x^\alpha L_k^\alpha(x)L_{k'}^\alpha(x)dx = \frac{\Gamma(\alpha + k + 1)}{k!} \delta_{k,k'}. \quad (17)$$

We recover the standard solutions for the radial hydrogenic eigenfunctions when $\alpha_{nl} = 1$, giving $E_0 = -Z^2/2n^2$. Notice that λ (and therefore E_0) is fixed for the Coulomb Sturmians whereas $\lambda = \sqrt{-2E_0}$ depends upon n for the Schrödinger eigenfunctions.

Much of the utility of the Coulomb Sturmians derives from the ease of computing matrix elements such as

$$\langle kl|x^p|k'l \rangle = \int_0^\infty s_{kl}(x)x^p s_{k'l}(x)dx$$

for integer values of p , which can be used to construct finite matrix representations of hydrogenic operators. In particular when $p = -1$,

$$\langle kl|x^{-1}|k'l \rangle = \frac{(2l + k + 1)!}{k!} \delta_{k,k'}, \quad (18)$$

which agrees with (17) if we put $\alpha = 2l + 1$ and $k = n - l - 1$. The Gram (overlap) matrix, G , is derived from the case $p = 0$. Choosing the normalization

$$\mathcal{N}_{nl} = \left[\frac{(n - l - 1)!}{2n(n + l)!} \right]^{1/2}, \quad (19)$$

gives non-vanishing elements of the Gram matrix

$$g_{nm}^l = 1, \quad g_{n,n+1}^l = g_{n+1,n}^l = -\frac{1}{2} \sqrt{1 - \frac{l(l+1)}{n(n+1)}}, \quad n = l + 1, l + 2, \dots \quad (20)$$

Although the Coulomb Sturmians are orthogonal with respect to the weight function $x^{-1/2}$, it is usually preferable to use them unweighted, in which case the treatment of completeness and linear independence is more complicated. The classical proof that the orthonormal system $(2/x)^{1/2}S_{nl}(x)_{n=l+1}^\infty$ is complete in $L^2(\mathbf{R}_+)$ is given by [19]. It follows that if we define the functions on $\mathbf{R}^3 \rightarrow \mathbf{R}$ by

$$\phi_{nlm}(\mathbf{r}) = \frac{S_{nl}(r)}{r} Y_{lm}(\theta, \varphi), \quad n \geq l + 1, \quad |m| \leq l,$$

where (r, θ, φ) are spherical polar coordinates of the position \mathbf{r} and $Y_{lm}(\theta, \varphi)$ are spherical harmonics, then the set $\{(2/r)^{1/2}\phi_{nlm}(\mathbf{r})\}$ is a complete orthonormal system in $L^2(\mathbf{R}^3)$ [14]. The set $\{\phi_{nlm}(x)\}$ is also minimal and complete on the Sobolev spaces $W_2^{(p)}(\mathbf{R}^3)$ for $p = 1, 2$, which proves to be exactly what is needed for convergence of the Rayleigh-Ritz method in atomic and molecular problems.

Gerschgorin's Circle Theorem [20] allows us to verify that the Gram matrix $G^{(N)}$ formed from the first N Coulomb Sturmians when $l > 0$ is positive definite. Since each eigenvalue, μ , of the tridiagonal Gram matrix is located in the union of intervals $1 - \rho_n \leq \mu \leq 1 + \rho_n$, where

$$\rho_n = |g_{n,n-1}| + |g_{n,n+1}|, \quad n = l + 1, l + 2, \dots, l + N$$

so that

$$\rho_n \sim 1 - \frac{l(l+1)}{n^2} + O(n^{-3}), \quad n \gg l + 1.$$

Thus all eigenvalues lie in the interior of the interval $(0, 2)$ so that every finite subset of the Coulomb Sturmians has a positive definite Gram matrix. The condition number of the matrix $G^{(N)}$ is $k_N = (1 + \rho_N)/(1 - \rho_N) \sim 2N^2/l(l+1)$ when $l > 0$ and N is large, so that the system is very well conditioned and there is little danger of linear dependence problems in practice. When $l = 0$, $g_{n,n+1} = -1/2$ independent of the value of n , but it is easy to show that $\det G^{(N)} \neq 0$ for all values of N so that we still have linear independence.

6 DIRAC L-SPINORS

The Dirac L-spinors are defined as relativistic analogues of the Coulomb Sturmians. We envisage representing Dirac four-component wavefunctions as linear combinations

$$\begin{bmatrix} \frac{1}{r} \sum_{n_r} c_{n_r}^L f_{n_r \kappa}^L(r) \chi_{\kappa m}(\theta, \varphi) \\ i \frac{1}{r} \sum_{n_r} c_{n_r}^S f_{n_r \kappa}^S(r) \chi_{-\kappa m}(\theta, \varphi) \end{bmatrix} \quad (21)$$

of form similar to that of (10).

In terms of the independent variable $x = 2\lambda r$, $\lambda > 0$ constant, the L-spinor amplitudes are given by the formulae [1, equations 22.146, 22.147]

$$\begin{aligned} f_{n_r \kappa}^L(x) &= \mathcal{N}_{n_r \kappa} x^\gamma e^{-x/2} \\ &\times \left\{ -(1 - \delta_{n_r, 0}) L_{n_r - 1}^{2\gamma}(x) + \frac{N_{n_r \kappa} - \kappa}{n_r + 2\gamma} L_{n_r}^{2\gamma}(x) \right\}, \end{aligned} \quad (22)$$

$$\begin{aligned} f_{n_r \kappa}^S(x) &= \mathcal{N}_{n_r \kappa} x^\gamma e^{-x/2} \\ &\times \left\{ -(1 - \delta_{n_r, 0}) L_{n_r - 1}^{2\gamma}(x) - \frac{N_{n_r \kappa} - \kappa}{n_r + 2\gamma} L_{n_r}^{2\gamma}(x) \right\}. \end{aligned} \quad (23)$$

The labels L, S identify the “large” and “small” components of the Dirac spinor in a conventional way, n_r is a non-negative integer, and

$$\gamma = +\sqrt{\kappa^2 - Z^2/c^2}, \quad N_{n_r\kappa} = +\sqrt{n_r^2 + 2n_r\gamma + \kappa^2}, \quad (24)$$

are respectively the leading exponent of the power series expansion of the functions about $x = 0$ and the *apparent principal quantum number*. The L-spinors are solutions of the differential equation system³

$$\begin{bmatrix} \frac{1}{2} - \frac{\alpha_{n_r\kappa} Z \mu^2}{c} \frac{1}{x} & -\frac{d}{dx} + \frac{\kappa}{x} \\ \frac{d}{dx} + \frac{\kappa}{x} & -\frac{1}{2} - \frac{Z}{\alpha_{n_r\kappa} \mu^2 c} \frac{1}{x} \end{bmatrix} \begin{bmatrix} \mu^{-1} f_{n_r\kappa}^L(x) \\ \mu f_{n_r\kappa}^S(x) \end{bmatrix} = 0, \quad (25)$$

where c is the speed of light ($c \approx 137$ in atomic units), and μ^2 is a root of the equation

$$\mu^4 - \frac{2c}{\lambda} \mu^2 + 1 = 0. \quad (26)$$

We choose

$$\mu^2 = \frac{c}{\lambda} \left(1 + \sqrt{1 - \frac{\lambda^2}{c^2}} \right), \quad \mu^{-2} = \frac{c}{\lambda} \left(1 - \sqrt{1 - \frac{\lambda^2}{c^2}} \right).$$

which ensures that $f_{n_r\kappa}^L(x) \rightarrow \text{const.}$ $S_{n_r l}(x)$ in the nonrelativistic limit $c \rightarrow \infty$ which we study below.

The analogue of the nonrelativistic energy parameter $E_0 = -\lambda^2/2$ is given by

$$E_0^R = c^2 \sqrt{1 - \lambda^2/c^2} = c^2 + E_0 + O(1/c^2). \quad (27)$$

The boundary conditions as $r \rightarrow 0$ and $r \rightarrow \infty$ are satisfied when

$$\alpha_{n_r\kappa} = N_{n_r\kappa} \lambda / Z$$

and the L-spinor amplitudes coincide with Dirac-Coulomb eigenfunctions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ having principal quantum number $n = n_r + |\kappa|$ when $\alpha_{n_r\kappa} = 1$.

In the nonrelativistic limit (in which light travels with infinite speed, $c \rightarrow \infty$),

$$f^L(x) \rightarrow \text{const.} \quad S_{nl}(x)$$

for both signs of κ whilst

$$f^S(x) \rightarrow \text{const.} \quad \left(\frac{d}{dx} + \frac{\kappa}{x} \right) x^{l+1} e^{-x/2} L_{n_r}^{2l+1}(x),$$

³The brief summary of L-spinors in [1, §(22.6.3)] is correct save for equation (22.145), which should be replaced by the present equation (25).

which may be expressed in terms of the criterion of *strict kinetic balance*

$$\lim_{c \rightarrow \infty} f^S(x) = \text{const.} \left(\frac{d}{dx} + \frac{\kappa}{x} \right) f^L(x).$$

This ensures that the representation by L-spinors is consistent with the well-known Pauli approximation in the nonrelativistic limit [21].

The calculation of L-spinor matrix elements proceeds along similar lines to the calculation of Coulomb Sturmian matrix elements. The normalization factor $\mathcal{N}_{n_r, \kappa}$, the same for both $f_{n_r, \kappa}^L(x)$ and $f_{n_r, \kappa}^S(x)$, is given by

$$\mathcal{N}_{n_r, \kappa} = \left[\frac{n_r! (2\gamma + n_r)}{2N_{n_r, \kappa} (N_{n_r, \kappa} - \kappa) \Gamma(2\gamma + n_r)} \right]^{1/2}, \quad (28)$$

and the tridiagonal Gram matrix has elements

$$\begin{aligned} g_{n_r, n_r}^{\kappa} &= 1, \\ g_{n_r, (n_r+1)}^{(\kappa)} &= g_{(n_r+1), n_r}^{(\kappa)} = \frac{\eta^T}{2} \left[\frac{(n_r + 1)(2\gamma + n_r + 1)(N_{n_r, \kappa} - \kappa)}{N_{n_r, \kappa} N_{(n_r+1), \kappa} (N_{(n_r+1), \kappa} - \kappa)} \right]^{1/2}, \quad T = L, S \end{aligned} \quad (29)$$

where $\eta^L = -1$ and $\eta^S = +1$. The large component matrix reduces correctly to that of Coulomb Sturmians in the nonrelativistic limit, and has very similar properties. Both L and S L-spinor sets are complete and minimal on the Sobolev spaces $[W_2^{(p)}(\mathbf{R}^3)]^2$ for $p = 1, 2$, exactly what is needed for constructing trial wavefunctions for Rayleigh-Ritz approximation of Dirac four-component wavefunctions.

One of the most important symmetries of the Dirac equation is charge conjugation which, loosely speaking, sets up a correspondence between electron and positron states. Under charge conjugation, Dirac four-spinors transform like

$$\psi \rightarrow \psi_c = C \bar{\psi}^t \quad (30)$$

where the superscript t denotes transposition and $\bar{\psi} = \psi^* \gamma^0$ is Dirac conjugation. The matrix C is given by

$$C = i\gamma^2 \gamma^0 = \begin{bmatrix} 0 & -i\sigma^2 \\ -i\sigma^2 & 0 \end{bmatrix}.$$

When the radial amplitudes $P(r), Q(r)$ are real, it is easy to show that if

$$\psi = \frac{1}{r} \begin{bmatrix} P(r) \chi_{\kappa, m} \\ iQ(r) \chi_{-\kappa, m} \end{bmatrix}$$

then

$$\psi_c = -i(-1)^{m+1/2} \begin{bmatrix} Q(r) \chi_{-\kappa, -m} \\ iP(r) \chi_{\kappa, -m} \end{bmatrix}$$

κ	k_N
-1	9203
1	4558
-2	4568
2	2815
-3	2813
3	884
-4	884
4	143
-5	143

 Table 1: Gram matrix condition numbers, k_N , for $Z = 100$ and $N = 100$

Under this transformation, expectation values of the position variable and the charge-current vector remain invariant, whilst those of spin, orbital and total angular momentum change sign, as does the sign of the energy parameter E and the sign of Z coupling the electron to the external Coulomb potential.

By making the corresponding changes

$$Z \leftrightarrow -Z, \quad f_{n_r\kappa}^L(x) \leftrightarrow f_{n_r\kappa}^S(x), \quad \kappa \leftrightarrow -\kappa, \quad \mu \leftrightarrow \mu^{-1}$$

in (25) we see that L-spinors retain the charge conjugation symmetries of the Dirac eigenfunctions on which they are modelled. Since the mapping $\mu \leftrightarrow \mu^{-1}$ is equivalent to changing the sign of the energy parameter $E_0^R = +\sqrt{1 - \lambda^2/c^2}$, (27), we infer that L-spinor expansions will be able correctly to represent positron (negative energy electron) states as well as bound states.

7 HYDROGENIC ATOMS IN AN L-SPINOR BASIS

From (11), the Galerkin equations for a hydrogenic atom are

$$\begin{bmatrix} c^2 \mathbf{S}^{LL} + \mathbf{V}^{LL} & c\mathbf{\Pi}^{LS} \\ c\mathbf{\Pi}^{SL} & -c^2 \mathbf{S}^{SS} + \mathbf{V}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} = E \begin{bmatrix} \mathbf{S}^{LL} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix}$$

Detailed formulae for the $N \times N$ blocks may be found elsewhere [22]. Here we note that the dependence on the ‘‘tuning parameter’’ λ is given by

$$\mathbf{\Pi}^{SL} = \mathbf{\Pi}^{LS} = \lambda\boldsymbol{\pi}, \quad \mathbf{V}^T = -\lambda\mathbf{v}^T, \quad \mathbf{S}^{TT} = \lambda\mathbf{g}^\kappa/2, \quad T = L, S. \quad (31)$$

The generalized eigenvalue problem has been solved using standard EISPACK routines with Fortran double precision arithmetic taking the speed of light $c = 137.0359895$ a.u. (the currently accepted value of the reciprocal fine structure constant). The results conform to the predictions of §5. The eigenvalues of the Gram matrices lie, as predicted,

Z	$\kappa = -1$	$\kappa = 1$	$\kappa = -2$	$\kappa = 2$	$\kappa = -3$
10	-552	-201	-201	-107	-107
20	-1117	-406	-402	-215	-215
30	-1708	-618	-607	-324	-323
40	-2342	-843	-815	-434	-432
50	-3039	-1086	-1028	-547	-542
60	-3827	-1355	-1248	-664	-653
70	-4748	-1663	-1476	-785	-767
80	-5868	-2026	-1715	-910	-883
90	-7296	-2476	-1966	-1042	-1002
100	-9243	-3069	-2232	-1181	-1123
110	-12176	-3928	-2517	-1328	-1249
120	-17440	-5407	-2823	-1487	-1378
130	-31921	-9286	-3157	-1657	-1512

Table 2: V_{min} in atomic units as a function of atomic number Z . The block dimension is $N = 100$. $-2mc^2 = -37557.7248$ a.u.

inside the interval $(0, 2)$. Condition numbers, k_N , for atomic number $Z = 100$, block dimension $N = 100$, and various symmetries, κ , Table 1, are similar to those of nonrelativistic Coulomb Sturmian basis sets of the same size. The lower bound on the bound state spectrum, V_{min} , obtained as the lowest eigenvalue of

$$\mathbf{V}^{TT} \mathbf{c} = v \mathbf{S}^{TT} \mathbf{c},$$

the same for $T = L$ and $T = S$, is shown in Table 2, confirming that $V_{min} > -2mc^2$ for all values of Z tabulated. the range of Z from $Z = 118$ to 137 is satisfied. We have successfully generated solutions when $|\kappa| = 1$ even for values of Z as close to critical as 137.035989 , where $V_{min} < -2mc^2$ though the accuracy is no longer very good. This should not cause surprise, as the condition $V_{min} > -2mc^2$ is sufficient, but not necessary. We can generate solutions for larger values of $|\kappa|$ up to $Z = c|\kappa|$ in the same way. The matrix diagonaliser produces ordered eigenvalues, in which those numbered $N + 1, N + 2, \dots, 2N$ correspond to the positive spectrum, and those numbered $1, \dots, N$ lie below $-2mc^2$. The case $Z = 50$, large enough to show some relativistic effects, appears in Table 3, showing rapid stabilization of the lowest eigenvalues as N increases. By choosing the tuning parameter $\lambda = Z/N_{n,r,\kappa}$, we represent the Dirac Coulomb $n_r\kappa$ eigenstate by a single L-spinor. Other eigenstates will be still represented by a non-trivial linear combination. However, the stable eigenvalues are insensitive to the choice of λ over a wide range: for example, the eigenvalues ϵ_{ns} , $n = 1 - 8$, are unchanged to 7 decimal places, when $30.0 \leq \lambda \leq 50.0$. The stabilized eigenvalues display the correct $|\kappa|$ degeneracy, $\epsilon_{2s} = \epsilon_{2p_{1/2}}$, $\epsilon_{3p_{3/2}} = \epsilon_{3d_{3/2}} \dots$, and the correct fine structure ordering. The $(N + 1)$ -th eigenvalue is always the lowest bound state of its symmetry and there are no spurious states, interlopers or pathological

N	ϵ_{1s}	ϵ_{2s}	ϵ_{3s}	ϵ_{4s}	ϵ_{5s}
20	-1294.62616	-326.494806	-143.829353	-79.5730938	-35.1391668
40	-1294.62616	-326.494806	-143.829802	-80.3703311	-51.1923424
60	-1294.62616	-326.494806	-143.829802	-80.3703316	-51.1977244
80	-1294.62616	-326.494806	-143.829802	-80.3703316	-51.1977244
	$\epsilon_{2p_{1/2}}$	$\epsilon_{3p_{1/2}}$	$\epsilon_{4p_{1/2}}$	$\epsilon_{5p_{1/2}}$	$\epsilon_{6p_{1/2}}$
20	-326.494806	-143.829807	-80.3703372	-51.1972465	-35.2027152
40	-326.494806	-143.829803	-80.3703331	-51.1977253	-35.433571
60	-326.494806	-143.829802	-80.3703323	-51.1977248	-35.4335707
80	-326.494806	-143.829802	-80.370332	-51.1977247	-35.4335706
100	-326.494806	-143.829802	-80.3703319	-51.1977246	-35.4335705
	$\epsilon_{2p_{3/2}}$	$\epsilon_{3p_{3/2}}$	$\epsilon_{4p_{3/2}}$	$\epsilon_{5p_{3/2}}$	$\epsilon_{6p_{3/2}}$
20	-315.144355	-140.457874	-78.952058	-50.4731861	-34.7554737
40	-315.144355	-140.457874	-78.952058	-50.4738674	-35.0157937
60	-315.144355	-140.457874	-78.952058	-50.4738674	-35.0157937
	$\epsilon_{3d_{3/2}}$	$\epsilon_{4d_{3/2}}$	$\epsilon_{5d_{3/2}}$	$\epsilon_{6d_{3/2}}$	$\epsilon_{7d_{3/2}}$
20	-140.457874	-78.9520581	-50.4738674	-35.0157937	-25.7034854
40	-140.457874	-78.952058	-50.4738674	-35.0157937	-25.7037387
60	-140.457874	-78.952058	-50.4738674	-35.0157937	-25.7037387

Table 3: Convergence with respect to matrix block dimension, N , for positive energy states of a hydrogenic atom with $Z = 50$. Tuning parameters – s -states: $\lambda = 50.0$; p -states: $\lambda = 25.0$; d -states: $\lambda = 15.0$.

behaviour characterized as “finite basis set disease” and “continuum dissolution” in such papers as [23].

The N -th eigenvalue of each symmetry is always the highest in the “negative energy sea” and is always safely below the upper bound $-2mc^2$. Since there are no bound states, we expect to see no convergent sequences of eigenvalues as N increases nor do we find any.

8 PERTURBATION PROBLEMS

Perturbation calculations using Rayleigh-Ritz generated wavefunctions require both that the matrix elements needed converge as the basis set is enlarged, and also that the N -dimensional spectrum spans the region that makes the dominant contribution to the perturbation sum. We illustrate this with a calculation of the second order static dipole polarizability α_{zz} for the state $|\psi_0\rangle$, energy ϵ_0 , of a hydrogenic atom:

$$\alpha_{zz} = 2 \sum_{n \neq 0} \frac{\langle \psi_0 | z | \psi_n \rangle \langle \psi_n | z | \psi_0 \rangle}{\epsilon_n - \epsilon_0}. \quad (32)$$

Z	$Z^4\Delta_{+1}$	N_{+1}	$Z^4\Delta_{-2}$	N_{-2}
1	6.749531	2	6.749676	2
5	6.738272	2	6.741888	2
10	6.703128	4	6.717556	2
15	6.644694	6	6.677018	2
20	6.563177	10	6.620296	3
30	6.332152	18	6.458439	3
40	6.013420	26	6.232346	3
50	5.611749	36	5.942529	4
60	5.133374	46	5.589629	4
70	4.586085	56	5.174405	3
80	3.979358	66	4.697663	5
90	3.324546	76	4.160097	6
100	2.635150	86	3.561882	6
110	1.927202	96	2.901526	5
120	1.219632	102	2.171964	10
130	0.532359	108	1.339899	16
135	0.192185	103	0.819494	22

 Table 4: Contributions, Δ_κ , eqn.(34), to the second order static polarizability of a hydrogenic atom.

In the Dirac case, the sum includes both positive and negative energy eigenstates. For brevity, we treat only the case in which ψ_0 is the $1s_{1/2}$ ground state; angular momentum selection rules then restrict the intermediate sum to states with p - symmetry, $\kappa = +1, \kappa = -2$. The matrices are diagonal with respect to j_z , so we can forget m_j dependence. After performing angular integrations, we get

$$\alpha_d = \frac{2}{9}(\Delta_{+1} + 2\Delta_{-2}) \quad (33)$$

We have compared our numerical results, Table 4, for Δ_{+1} and Δ_{-2} , obtained by computing the sums

$$\Delta_\kappa = \sum_{n \neq 0}^+ \frac{(0|r|n\kappa)(n\kappa|r|0)}{\epsilon_n - \epsilon_0} \quad (34)$$

with analytical formulae [24, equations (182)–(184)]. The sum over intermediate states runs over the whole pseudo-spectrum including both positive and negative energy states. The block dimensions, N_κ , have been adjusted so that

$$Z^4|\Delta_\kappa - \Delta_\kappa^{analytic}| \leq 10^{-6}; \quad (35)$$

Similar calculations at higher precision take longer to run. The results, Table 4, are relatively insensitive to the choice of λ , though the value of N needed to obtain a specific precision does change.

Z	ϵ_0	ϵ_2^+	ϵ_2^-	ϵ_2	$\epsilon_2, \text{ (eqn.37)}$
10	-50.066742	-0.504124	0.000103	-0.504021	-0.504021
20	-201.076523	-0.517050	0.000639	-0.516412	-0.516412
30	-455.524907	-0.539986	0.001761	-0.538225	-0.538225
40	-817.807498	-0.575014	0.003560	-0.571454	-0.571455
50	-1294.626156	-0.625644	0.006153	-0.619491	-0.619495
60	-1895.682356	-0.697763	0.009731	-0.688032	-0.688042
70	-2634.846565	-0.801543	0.014631	-0.786912	-0.786943
80	-3532.192151	-0.955598	0.021459	-0.934139	-0.934228
90	-4617.757654	-1.197084	0.031394	-1.165689	-1.165967
100	-5939.195384	-1.610319	0.047022	-1.563297	-1.564287

Table 5: Perturbed hydrogenic 1s state

The perturbed hydrogenic atom was first studied nonrelativistically by Rosky and Karplus [25]; it has the advantage that the states of the unperturbed system are known exactly, as is the final answer, so that the error at each order of perturbation is easy to establish. Since the nonrelativistic expression for the energy is quadratic in Z , the sum over all Feynman diagrams contributing to the energy of order k vanishes for $k > 2$. Diagrams of order $k \geq 3$ should sum to zero for each value of k . Rosky and Karplus found that integrating over continuum states is very inaccurate as integrals over the perturbation $-Z'/r$ which are diagonal in energy diverge. so that the energy integration needs to be done with care. We first showed [26] that the problem became quite straightforward, using simple finite basis sets of either exponential or Gaussian form and extended this to the Dirac case in [27]; the higher order diagrams of order $k \geq 3$ no longer sum to zero. Our most important conclusion was that the contribution of negative energy virtual states is essential to get good agreement with the perturbation series derived from Dirac's equation.

Here we treat the perturbed 1s level, for which we have the simple formula

$$\epsilon(Z) = (\gamma - 1)c^2, \quad \gamma = \sqrt{1 - Z^2/c^2}, \quad (36)$$

so that the perturbation series takes the form

$$\epsilon(Z + Z') = \epsilon(Z) + \epsilon_1(Z).Z' + \epsilon_2(Z).Z'^2 + \dots \quad (37)$$

where, using Taylor's theorem,

$$\epsilon_1(Z) = \epsilon'(Z) = -Z/\gamma, \quad \epsilon_2(Z) = \frac{1}{2}\epsilon''(Z) = -1/2\gamma^3, \dots$$

which clearly agrees with the nonrelativistic result in the limit $c \rightarrow \infty$. In the finite

dimensional formulation, we have to evaluate the expressions

$$\epsilon_1(Z) = \langle \psi_0 | 1/r | \psi_0 \rangle, \quad \epsilon_2(Z) = \sum_{n \neq 0} \frac{\langle \psi_0 | 1/r | \psi_n \rangle \langle \psi_n | 1/r | \psi_0 \rangle}{\epsilon(Z) - \epsilon_n(Z)} \quad (38)$$

where $\epsilon_n(Z)$ is the eigenvalue associated with $|\psi_n\rangle$, the sum extending over the complete spectrum of positive and negative energy states. Table 5 displays the results computed with block dimension $N = 100$ taking $\lambda = Z$ to be fixed. This is not sufficient for the highest values of Z ; the difference between the sum over states in the penultimate column and the exact value in the last column gives some idea of the error. The negative energy state contribution grows roughly like Z^3 , and is clearly non-negligible for high Z , demonstrating that any perturbation of the Dirac Hamiltonian, whether one-electron or two-electron, contains contributions from unperturbed negative energy states. Thus attempts to solve many-electron problems using methods which attempt to project out negative energy contributions [23] always introduce unquantifiable errors as well as formidable technical complications.

9 DISCUSSION

We have provided evidence that there is no insuperable problem in applying variational methods in a straightforward way to relativistic electronic structure problems in atoms, molecules or condensed matter. The energy projection operators recommended almost universally in the literature (e.g. [23]) are not only unnecessary but introduce unquantifiable errors into the calculation. This greatly simplifies the solution of many-electron problems, provided the basis sets are chosen to satisfy the right boundary conditions and limiting behaviour [1], exemplified by the L-spinors used in this paper. Since the regions near the nuclei are the source of relativistic dynamical effects, it is important to ensure that the trial functions have the correct spinor structure there, something more elaborate than the simple cusp conditions used automatically in nonrelativistic calculations. The S-spinors [1, p. 279], derived from the L-spinors, have the correct behaviour near a point nucleus, and have been used effectively in many atomic calculations [11, 28, 29]. Molecular calculations are most easily done using Gaussian functions, and we have devised the G-spinors for this purpose [1, p. 280]. Whilst the molecular program BERTHA is still being developed, its principles have been described in several articles such as [30, 31], and there have been a number of applications to molecular structure and to the calculation of electromagnetic properties [30, 31, 32, 33]. Work is in hand to extend the algorithms to relativistic density functional theory with the aim of ensuring that relativistic methods based on Dirac Hamiltonians may soon take their place in the toolkit of computational physicists and chemists.

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The Rayleigh-Ritz method is a numerical method of finding approximations to eigenvalue equations that are difficult to solve analytically, particularly in the context of solving physical boundary value problems that can be expressed as matrix differential equations. It is used in mechanical engineering to approximate the eigenmodes of a physical system, such as finding the resonant frequencies of a structure to guide appropriate damping. The name is a common misnomer used to describe the method that

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