A variational method for relativistic computations in atomic and molecular physics

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Abstract. This paper is devoted to the numerical computation of energy levels of Dirac operators with applications in atomic and molecular physics. Our approach is based at a theoretical level on a rigourous variational method. This provides a numerical method which is free of the numerical drawbacks which are often present in discretized relativistic approaches. It is moreover independent of the geometry and monotone: eigenvalues are approximated from above. We illustrate our numerical approach by the computation of the ground state in atomic and diatomic configurations using B-splines.

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Key Words : Quantum chemistry – relativistic quantum mechanics – relativistic models for atoms and molecules – computational methods – ab-initio methods – basis sets – B-splines – Dirac operators– effective Hamiltonians – variational methods – min-max – minimization – continuous spectrum – eigenvalues – Rayleigh-Ritz technique – minimization – variational collapse – spurious states

The numerical computation of one-particle bound states of Dirac equations is difficult due to the unboundeness of the free Dirac operator. Several numerical drawbacks are present in most of the computational techniques. Various approaches based for instance on squared Dirac operators [25, 1], min-max formulations [23, 4], use of special basis sets [7, 17, 15, 12] or even more elaborated methods have been proposed [11, 8], as well as perturbative corrections to non-relativistic models and derivation of effective Hamiltonians (see for instance [18, 16, 21, 22, 3, 10, 19, 20]). None of these remedies provides a complete and satisfactory answer. From a numerical viewpoint, the *variational collapse* or the *dissolution into the continuous spectrum* and the existence of *spurious states* [14, 9] are serious problems which have been solved in special cases by taking appropriate projections or imposing additional conditions, for instance on a boundary [7].

In [5] we proposed an exact and stable numerical method based on a new variational reduction of the problem to 2-spinorial functions with an application to the computation of spherically symmetric ground states. Here we explain the theoretical basis of our approach and then precisely describe how to use this method in atomic or molecular computations. Numerical results for hydrogenoid ions corresponding to atomic or diatomic configurations are given. We do not pretend to give accurate numerical results and this is actually not the purpose of this paper. For instance, we use meshes with constant steps, which are clearly not optimal. The main point is that the method does not rely on any special geometry and has interesting numerical features: none of the above mentioned difficulties occurs and eigenvalues are approximated monotonically from above. Moreover, it is numerically tractable and robust, in the sense that no special information on the solutions needs to be injected in order to provide reliable results.

It is well known that the eigenvalues of an operator H can be obtained as critical values of the Rayleigh quotient

$$Q(\psi) := \frac{(H\psi, \psi)}{(\psi, \psi)}\,.$$

In the case of operators which are bounded from below, with eigenvalues below the continuum, the infimum of the quotient Q is the ground state energy. However the Dirac operator is totally unbounded. Hence, the same minimization would take us to $-\infty$. One possible way out consists in minimizing the Rayleigh quotient on a subspace of spinors which correspond to electronic states and for which the quotient is bounded from below. In this case one is actually solving the eigenvalue equation $\Lambda H \Lambda\, \psi = E\, \psi$, where H

is now the Dirac operator and Λ the projector onto the orthogonal to the subspace corresponding to the negative continuous spectrum of H. However, Λ is in general unknown and replacing it by an approximation introduces many difficulties. The method is for instance very dependent on the potential. In the case of nonlinear problems for which the solutions are obtained by iteration of linearized ones, the potentials change at every step, which may cause serious numerical unconsistencies.

Here we propose a method which is based on a minimization procedure, but not a direct minimization of the Rayleigh quotient of course. First we eliminate the lower spinor to obtain a second order equation for the upper one. The reduced Hamiltonian is then *eigenvalue dependent*. After a further step, we finally reduce the question to that of *solving a nonlinear scalar equation*. The method applies not only to the *ground state* but also to the wave functions corresponding to *excited levels*.

In the litterature one finds many works dealing with the construction of *effective operators* which share the positive eigenvalues of the Dirac operators, but are bounded from below. One way of constructing them is to use projectors. Formally, if Λ^+ is the positive spectral projector associated with H, the equation

$$\Lambda^+ H \Lambda^+ \psi = E\psi$$

will indeed have the good properties of sharing with H all its positive eigenvalues and having no negative spectrum. Of course the projector Λ^+ is not known in closed form. In some sense, our method does it in an implicit manner.

Let us now come to the particular case of the Dirac operator $H = H_0 + V$, where H_0 is given by $H_0 = -i\,\alpha \cdot \nabla + \beta$ and V is a fixed scalar potential. The units have been chosen so as to have $m = c = \hbar = 1$ and $\alpha_1, \alpha_2, \alpha_3, \beta$ are the Pauli-Dirac matrices. If we write any 4-spinor ψ as $\psi = \binom{\varphi}{\chi}$, with φ, χ taking values in $\mathbb{C}^2$, the eigenvalue equation

$$H\,\psi = \lambda\,\psi$$

is equivalent to the system

$$\left\{ \begin{array}{rcl} R\,\chi &=& (\lambda - c^2 - V)\,\varphi \\ R\,\varphi &=& (\lambda + c^2 - V)\,\chi \end{array} \right. \qquad (1)$$

with $R = -i\,c\,(\vec{\sigma}.\vec{\nabla}) = -i\,c\,\sum_{k=1}^{3} \sigma_k\,\partial/\partial x_k$ where σ_1, σ_2, σ_3 are the Pauli matrices. Then, if ψ is an eigenfunction of H associated with the eigenvalue λ, and if the function $\lambda+c^2-V$ is never equal to 0, we have:

$$\chi = (\lambda + c^2 - V)^{-1} R\varphi \,, \tag{2}$$

and

$$R\left(\frac{R\varphi}{\lambda + c^2 - V}\right) = (\lambda - c^2 - V)\,\varphi \,. \tag{3}$$

The above equation, which can be found in several papers as, usually, a first step of an expansion procedure, is not linear in λ since the Hamiltonian acting on the upper spinor φ depends nonlinearly on it. However, multiplying (3) by φ and integrating with respect to $x \in \mathbb{R}^3$, we get :

$$\int_{\mathbb{R}^3} \left(\frac{|R\varphi|^2}{\lambda + c^2 - V} + (V + c^2 - \lambda)\,|\varphi|^2 \right) dx = 0 \,. \tag{4}$$

It is straightforward to check that for any given *admissible* 2-spinor φ, *i.e.* a spinor for which the integral of the above equation is well defined, there is a unique λ satisfying (4). Let us denote it by $\lambda(\varphi)$. In [6] we proved that for a large class of potentials V including the usual potentials arising in atomic and molecular physics, the ground state energy of the operator H (that we denote by λ_1) is the minimal value of $\lambda(\varphi)$ over all possible functions φ such that $R\varphi$ and ϕ are square integrable:

$$\lambda_1 = \inf_{\varphi} \ \lambda(\varphi) \,. \tag{5}$$

In this manner we have managed to minimize the Rayleigh quotient over all bound states of H and we have found the lowest eigenvalue of H in the gap $(-1, 1)$, or $(-c^2, c^2)$ in atomic units.

In order to design an efficient algorithm for the computation of λ_1, we may reformulate the question as follows. Let $A(\lambda)$ be the operator defined by the quadratic form acting on 2-spinors:

$$\int_{\mathbb{R}^3} \left(\frac{|R\varphi|^2}{\lambda + c^2 - V} + (V + c^2 - \lambda)\,|\varphi|^2 \right) dx =: (\varphi, A(\lambda)\varphi)$$

and consider its lowest eigenvalue, $\mu_1(\lambda)$. Because of the monotonicity of $A(\lambda)$ with respect to λ, there exists at most one λ for which $\mu_1(\lambda) = 0$. This λ is the ground state level λ_1.

An algorithm to numerically solve the above problem has been proposed in [5]. Consider the following approximation procedure for λ_1. Take any complete countable basis set $\mathcal{B}$ in the space of admissible 2-spinors X and let $\mathcal{B}_n$ be an n-dimensional subset of $\mathcal{B}$ generating the space X_n (we assume that $\mathcal{B}_n$ is monotone increasing in the sense that if $n < n'$, then $\mathcal{B}_n$ is contained in $\mathcal{B}_{n'}$). Denote by $\varphi_1, \varphi_2, \ldots, \varphi_n$ the elements of $\mathcal{B}_n$. For all $1 \le i, j \le n$, we define the $n \times n$ matrix $A_n(\lambda)$ whose entries are

$$(6) \qquad A_n^{i,j}(\lambda) = \int_{\mathbb{R}^3} \Big(\frac{(R\,\varphi_i, R\,\varphi_j)}{\lambda + c^2 - V} + (V + c^2 - \lambda)\,(\varphi_i, \varphi_j) \Big)\, dx\,,$$

where by (f, g) we denote the complex inner product of f by g. The matrix $A_n(\lambda)$ is selfadjoint and has therefore n real eigenvalues. We compute $\lambda_{1,n}$ as the solution of the equation

$$(7) \qquad \mu_{1,n}(\lambda) = 0\,,$$

where $\mu_{1,n}(\lambda)$ is the first eigenvalue of $A_n(\lambda)$. Note that the uniqueness of such a λ comes from the monotonicity of the l.h.s. of equation (4). Moreover, since for a fixed λ

$$(8) \qquad \mu_{1,n}(\lambda) \searrow \mu_1(\lambda) \quad \text{as} \quad n \to +\infty\,,$$

we also have

$$(9) \qquad \lambda_{1,n} \searrow \lambda_1 \quad \text{as} \quad n \to +\infty\,.$$

Another way to see why (9) holds is the following. The solution $\lambda_{1,n}$ of (7) is the minimum value of $\lambda(\varphi)$ among all the functions φ in X_n, which again proves the result if X_n approximates X as n goes to $+\infty$, or, in other words, if $\mathcal{B}_n$ converges to $\mathcal{B}$.

Note that all that has been said about the lowest eigenvalue and the ground state energy can be also said for the higher eigenvalues corresponding to excited states. Indeed, the (unique) root of the function which to λ associates $A_n(\lambda)$'s i-th eigenvalue is an (upper) approximation to the i-th exact eigenvalue of H. For a given i we can either look for the λ such that $\mu_i(\lambda) = 0$ or use another algorithm yielding all the λ_i's at the same time.

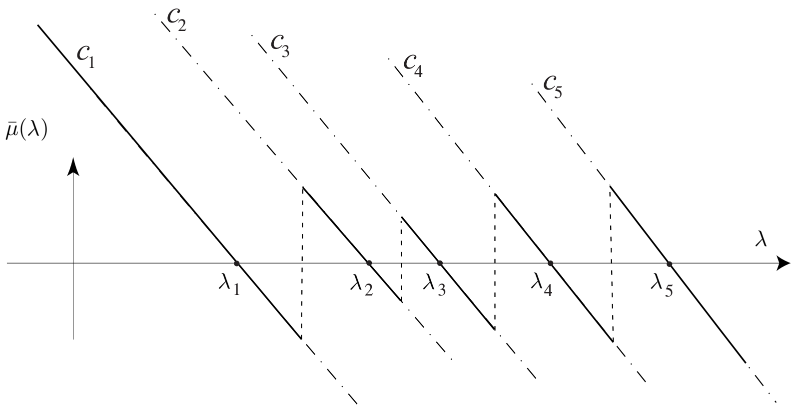

Figure 1: *Each eigenvalue $\mu_i(\lambda)$ of $A(\lambda)$, considered as a function of λ, is monotone decreasing. By looking for the zeros of the non continuous function $\lambda \mapsto \bar\mu(\lambda) = \inf_i |\mu_i(\lambda)|$, we obtain an efficient algorithm to compute all eigenvalues of the Dirac operator in the gap $(-1, 1)$ and the corresponding eigenfunctions. The ground state of course corresponds to the smallest zero of $\bar\mu(\lambda)$ in $(-1, 1)$. Moreover the method forbids variational collapse, no spurious states may appear and the only consequence of the approximation on a finite basis set is that eigenvalues are approximated from above.*

Our previous paper [5] contained some numerical results concerning the use of our method for finding the ground state energy for some Dirac operators in case of a spherical symmetry. The elements of the basis set used in [5] were Hermite functions. In this paper we discuss more efficient numerical results based on the use of B-spline function sets. The interest of using well localized basis set functions is the sparseness and the nice structure of the corresponding discretized matrix $A_n(\lambda)$. If the degree of the basis of B-splines increases, the number of filled diagonals will also increase. So, a good balance has to be found between the smoothness of elements of the approximating basis set and the speed of the corresponding numerical computations.

In the particular case of a central potential V (atomic case) (see for instance [24, 2]) our method can be made more precise and above all, the computations become much easier since one can reduce the whole problem to a one-dimensional one. Indeed, the bound states can be expressed in terms of the spherical harmonics:

$$\psi = \frac{1}{r}\begin{pmatrix} u_\kappa(r)\,\chi_{\kappa m}(\theta,\varphi) \\ i\,v_\kappa(r)\,\chi_{-\kappa m}(\theta,\varphi) \end{pmatrix}, \tag{10}$$

The dependence on the angular coordinates is contained in the 2-spinors $\chi_{\pm\kappa m}(\theta,\varphi)$, which are eigenfunctions of the angular momentum operators J, its third component J_z (with eigenvalues $(j(j+1)$ and m respectively) and of parity. On the other hand, the radial dependence is contained in the functions f and g which are called the upper and lower radial components of ψ.

In the ansatz (10), for a given $\kappa = \pm(j+\frac{1}{2})$, with $j = \ell \mp \frac{1}{2}$, $l = 0, 1, \ldots$, the operator H reduces to partial wave Dirac operators h_κ acting on the space $(L^2(0,+\infty))^2$ of pairs of square integrable real functions on $(0,+\infty)$:

$$h_\kappa = \begin{pmatrix} c^2+V & -c\frac{d}{dr}+\frac{c\kappa}{r} \\ c\frac{d}{dr}+\frac{c\kappa}{r} & -c^2+V \end{pmatrix} \quad (\kappa = \pm 1,\ \pm 2, \ldots) \tag{11}$$

In this context, for each κ, equation (4) which defines $\lambda(\varphi)$ becomes

$$\int_0^{+\infty} \frac{|(r^\kappa u(r))'|^2}{r^{2\kappa}(c^2+\lambda-V(r))}\,dr + \int_0^{+\infty} (c^2-\lambda+V(r))\,|u(r)|^2\,dr = 0\,. \tag{12}$$

For hydrogenic atoms we find the $1s$ state, *i.e.* the lowest energy state, in the case $\kappa = -1$ and for a given finite dimensional basis set $\{B_i, \ldots, B_n\}$, the entries of the matrix to consider are

$$\int_0^{+\infty} \frac{(r^\kappa B_i(r))'(r^\kappa B_j(r))'}{r^{2\kappa}(c^2+\lambda-V(r))}\,dr + \int_0^{+\infty} (c^2-\lambda+V(r))\,B_i(r)B_j(r)\,dr = 0\,. \tag{13}$$

Let us now come to the basic numerical computations that we have performed to *illustrate* our method. In Table 1 below we show some results that we have obtained in the case of the hydrogenoid atoms H, He^+, Cr^{23+} and Th^{89+}. We have considered B-splines of order 2 which produce tridiagonal matrices. The monotonicity of the approximation procedure is evident. We do not try to obtain optimal results and only intend to show the feasability of the numerical implementation of our approach and its good properties.

Basis dimension	H	He^{+}	Cr^{23+}	Th^{89+}
50	0.99997376	0.99989506	0.98478952	0.76513329
100	0.99997348	0.99989391	0.98461144	0.75833759
500	0.99997337	0.99989351	0.98454726	0.75448807
1000	0.99997337	0.99989349	0.98454513	0.75423687
2000	0.99997337	0.99989349	0.98454459	0.75414924
∞	0.99997337	0.99989349	0.98454439	0.75410233

Table 1: *The approximated value of the ground state level converges to the exact eigenvalue as the size of the basis set tends to* ∞. *These computations have been made by regularly distributing the splines in the interval* $(0, r_{\max})$, *with* $r_{\max} = 10/(Z\alpha)$ *and* $\alpha = 1/137.037$. *The size* $r_{\max}$ *of the interval has been chosen so that we do not lose much information by performing the computations in a finite domain. The units are chosen so that* $m = c = \hbar = 1$.

Instead of changing the basis dimension for a fixed $r_{\max}$, we may take different values of $r_{\max}$ and of spline widths $2\,h$. The results are given in Table 2. Again we verify that the approximation of the ground state level is monotone decreasing as $r_{\max}$ increases and that the value of $r_{\max}$ taken in Table 2 is a reasonable choice.

$\boxed{Z=1}$	h	20	10	5	1
$r_{\max}$					
700		0.9999737	0.9999735	0.9999735	0.9999735
800		0.9999736	0.9999734	0.9999734	0.9999734
$\boxed{Z=90}$	h	0.4	0.2	0.1	0.05
$r_{\max}$					
10		0.770385	0.760512	0.756478	0.754976
12		0.770310	0.760456	0.756428	0.754928

Table 2: *The quality of the approximating basis depends on two parameters: the basic step, i.e. the length, $2\,h$ of the support of the spline functions and the length of the interval $(0,\, r_{\max})$ on which we solve the Dirac equation. The exact eigenvalue is reached by taking simultaneously the limits $h \to 0$ and $r_{\max} \to +\infty$. We give here the computed values corresponding to $Z = 1$ (Hydrogen) and $Z = 90$ (Thallium). Exact values are respectively 0.99997337 and 0.75410233.*

When the potential V is not spherically symmetric, for instance in the case of molecules, the same kind of algorithm can be used, but the radial reduction is not possible anymore and we are forced to deal with computations in 2 or 3 dimensions. All the good properties of our algorithm remain the same in the molecular case, but of course the computational complexity becomes much higher, the basis sets being necessarily much larger. The matrices A_n will still be very sparse if a good localized basis and a good numbering of the basis set elements are chosen. Let us describe how to make the computations in the case of diatomic molecules. In this case, cylindrical symmetry allows us to reduce the space dimension to 2. Another feature is that one has to deal with 2-spinors: we cannot get rid of the lower part of the upper spinor. If we choose the cylindrical ansatz

$$\begin{pmatrix} f(s,z)\, e^{i(m-1/2)\phi} \\ i\, g(s,z)\, e^{i(m+1/2)\phi} \end{pmatrix}$$

for the 2-spinor φ, and if we consider the scalar finite basis set $\{B_1, \dots B_n\}$ and the case $m = 1/2$ (where the lowest energy corresponds to the energy $1(1/2)g$ of the molecules), the matrix $A_n(\lambda)$ can be decomposed in four blocks:

$$A_n = \begin{pmatrix} A_n^{11} & A_n^{12} \\ {}^t A_n^{12} & A_n^{22} \end{pmatrix} ,$$

where the entries of the three matrices A_n^{11} and A_n^{22} are respectively

$$\int_0^{+\infty} \int_{-\infty}^{+\infty} \left\{ \frac{\partial_s B_i \, \partial_s B_j + \partial_z B_i \, \partial_z B_j}{\lambda + c^2 - V} + (V + c^2 - \lambda)\, B_i B_j \right\} s \, ds \, dz \, ,$$

$$\int_0^{+\infty} \int_{-\infty}^{+\infty} \left\{ \frac{(\partial_s B_i + \frac{B_i}{s})\, (\partial_s B_j + \frac{B_j}{s}) + \partial_z B_i \, \partial_z B_j}{\lambda + c^2 - V} + (V + c^2 - \lambda)\, B_i B_j \right\} s \, ds \, dz \, .$$

and those of A_n^{12},

$$\int_0^{+\infty} \int_{-\infty}^{+\infty} \left\{ \frac{\partial_z B_i \, (\partial_s B_j + \frac{B_j}{s}) - \partial_s B_i \, \partial_z B_j}{\lambda + c^2 - V} \right\} s \, ds \, dz \quad (i \leq j) \, ,$$

$$\int_0^{+\infty} \int_{-\infty}^{+\infty} \left\{ \frac{(\partial_s B_i + \frac{B_i}{s})\, \partial_z B_j - \partial_z B_i \, \partial_s B_j}{\lambda + c^2 - V} \right\} s \, ds \, dz \quad (i > j) \, ,$$

One can choose basis sets and numbering of its elements such that any of the above matrices has nonzero elements only on some diagonals (their number depending again on the overlapping of the basis elements).

In order to illustrate our method in the molecular case, we have chosen to make some computations for the molecules H_2^+ and Th_2^{179+}. The first one corresponds to the case of light nucleii and the second one, to the case of heavy ones. In order to compare 1- and 2-dimensional computations, we have also used our algorithm in cylindrical coordinates to compute an approximation for the ground state energy of the hydrogenic atom Th^{89+}. Table 3 below contains the results of these numerical computations.

	Z	*Number of atoms*	$s_{\max}$	$z_{\max}$	h	$\lambda_{1,\max}$
Th^{89+}	90	1	10	10	0.4	0.774105
Th^{89+}	90	1	10	10	0.2	0.762610
Th^{89+}	90	1	∞	∞	0	0.754102
H_2^+	1	2	700	820	20	0.99994179
Th_2^{179+}	90	2	10	12	0.4	0.517343

Table 3: *Here are given some estimates of the ground state level in cylindrical coordinates* $(s = (x_1^2+x_2^2)^{1/2},\ z = x_3)$ *restricted to an interval* $(0, s_{\max})\times(-z_{\max}, z_{\max})$. *The purpose is simply to illustrate the method. Note that the approximate eigenvalues are upper estimates of* λ_1 *and monotonically decreasing functions of the size of the basis. The computation has been performed with B-splines of order 2 and support of size* $2\,h$, *which corresponds to a grid with constant step* h *and matrices of size* $O(h^{-2}) \times O(h^{-2})$ *with only* $O(h^{-2})$ *nonzero elements. No special information on the shape of the exact solution has been injected into the code. The choice of* $s_{\max}$ *and* $z_{\max}$ *has been made after observing the results contained in Table 2.*

Of course, much more precise computations have already been obtained for the same molecules. See, for instance, Kullie and Kolb [13] who use high accuracy finite element methods (FEM) and sophisticated elliptical coordinates for diatomic molecules, in order to better treat the nuclear singularities. It would be interesting to adapt their ideas to our framework.

Finally, to illustrate our computations, we show at the end of this paper the plots corresponding to Th^{89+}, H_2^+ and Th_2^{179+}. In each case a transversal plot of the density $|\varphi|^2$ at $s = h$ and a plot in (s, z) coordinates are given.

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References

[1] W.E. Baylis, S.J. Peel. Phys. Rev. A **28**, 2552 (1983).

[2] J.D. Bjorken, S.D. Drell. *Relativistic Quantum Mechanics.* McGraw-Hill, 1964.

[3] Ch. Chang, J.-P. Pelissier, Ph. Durand. Phys. Scripta **34**, 394 (1986).

[4] S.N. Datta, G. Deviah. Pramana, **30(5)**, 397(1988).

[5] J. Dolbeault, M.J. Esteban, E. Séré, M. Vanbreugel. Phys. Rev. Letters **85(19)**, 4020 (2000).

[6] J. Dolbeault, M.J. Esteban, E. Séré. J. Funct. Anal. **174**, 208 (2000).

[7] G.W.F. Drake, S.P. Goldman. Phys. Rev. A **23**(5), 2093 (1981).

[8] G.W.F. Drake, S.P. Goldman. Adv. Atomic Molecular Phys. **25**, 393(1988).

[9] I.P. Grant. A.I.P. Conf. Proc. P.J. Mohr, W.R. Johnson, J. Sucher eds. **189**, 235 (1989).

[10] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, A.-M. Mårtensson-Pendrill. J. Phys. B **19**, 2799 (1986).

[11] R.N. Hill, C. Krauthauser. Phys. Rev. Lett. **72(14)**, 2151 (1994).

[12] W. R. Johnson, S. Blundell, J. Sapirstein. Phys. Rev. A **37(2)**, 307 (1988).

[13] O. Kullie, D. Kolb. Preprint.

[14] W. Kutzelnigg. International J. Quantum Chem. **XXV**, 107 (1984).

[15] W. Kutzelnigg. Int. J. Quant. Chem. **25**, 107 (1984).

[16] W. Kutzelnigg. Z. Phys. D - Atoms, Molecules and Clusters **15**, 27 (1990).

[17] W. Kutzelnigg. Chemical Physics **225**, 203 (1997).

[18] W. Kutzelnigg. J. Chem. Phys. **110(17)**, 8283 (1999).

[19] E. van Lenthe, R. van Leeuwen, E.J. Baerends, J.G. Snijders. Publications Dept. Chem. Phys. and Material sciences. University of Groningen, 1994.

[20] R. van Leeuwen, E. van Lenthe, E.J. Baerends, J.G. Snijders. J. Chem. Phys. **101(2)**, 1272 (1994).

[21] A. Rutkowski, W.H.E. Schwarz. J. Chem. Phys. **104(21)**, 8546 (1996).

[22] A. Rutkowski. Chem. Phys. Letters **307**, 259 (1999).

[23] J.D. Talman. Phys. Rev. Lett. **57(9)**, 1091 (1986).

[24] B. Thaller. *The Dirac Equation.* Texts and Monographs in Physics. Springer-Verlag, Berlin, 1st edition, 1992.

[25] H. Wallmeier, W. Kutzelnigg. Chem. Phys. Lett. **78**, 341 (1981).

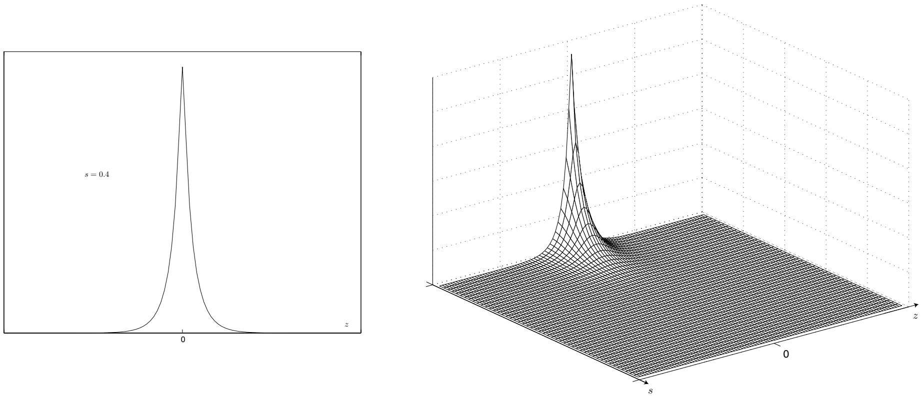

Figure 2: *Ground state of* Th^{89+} *corresponding to* $Z = 90$*, one atom, computed with* $s_{\max} = 10$*,* $z_{\max} = 10$*,* $h = 0.4$*.*

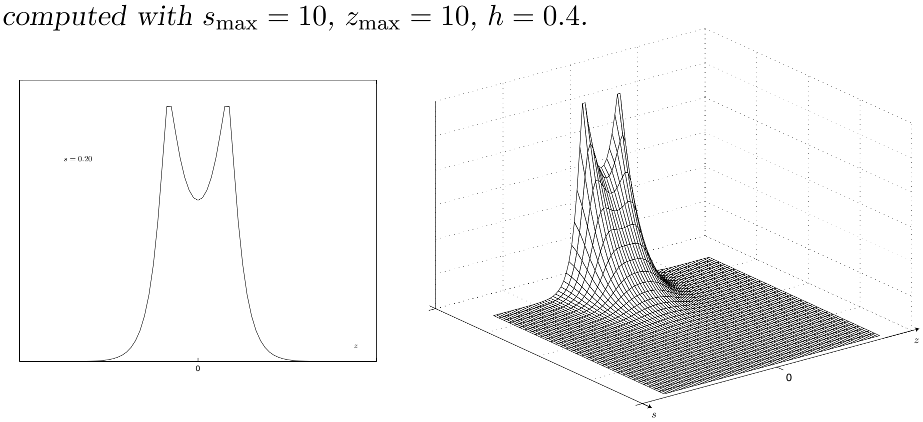

Figure 3: *Ground state of* H_2^+ *corresponding to* $Z = 1$*, two atoms, computed with* $s_{\max} = 700$*,* $z_{\max} = 820$*,* $h = 20$*.*

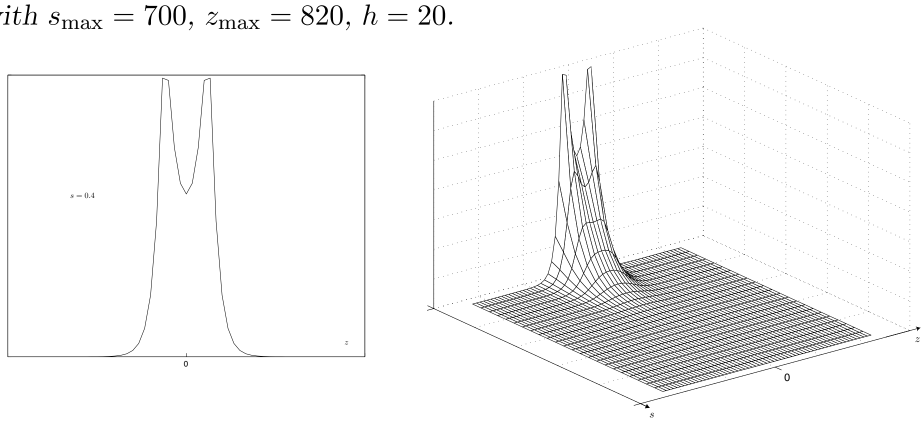

Figure 4: *Ground state of* Th_2^{179+} *corresponding to* $Z = 90$*, two atoms, computed with* $s_{\max} = 10$*,* $z_{\max} = 12$*,* $h = 0.4$*.*