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Finite basis set approach to two-center Dirac problem in Cassini coordinates

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Abstract. We lay out a new approach to solving the two-center Dirac eigenvalue problem. It is based on application of B-spline basis sets constructed in Cassini coordinates. The approach provides a very promising way for the theoretical description of various atomic processes such as charge transfer, excitation, ionization and electron-positron pair production, that accompany slow collisions of heavy ions. Moreover, yielding a (quasi) complete set of eigensolutions, the finite-basis-set method allows a systematic analysis of the quantum electrodynamics (QED) corrections to the energy levels of heavy quasi-molecules formed in these collisions.

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1. Introduction

Owing to recent advances in accelerator and storage ring techniques, new possibilities arise today to study formation of quasi-molecules in (relatively) slow heavy-ion collisions. In contrast to experimental studies performed during the last century, ion storage and cooler rings do allow nowadays to perform such experiments at arbitrary low beam energies for fully stripped or H-like ions interacting with high-Z neutral targets (Verma et al. 2005, Verma et al. 2006). For the future one may even anticipate slow collisions between high-Z bare and one-electron ions (FAIR 2001, Gumberidze et al. 2005, Stöhlker et al. 2007, Gumberidze et al. 2009). These quasi-molecules are known to be a versatile tool for investigating a number of fundamental problems in heavy-ion atomic physics (Betz et al. 1976, Müller 1976, Soff et al. 1977, Rafelski et al. 1978, Soff, Müller & Greiner 1978, Kirsch et al. 1978, Reinhardt et al. 1979, Soff et al. 1979, Müller et al. 1983, Soff et al. 1987, Müller-Nehler & Soff 1994). In particular, analysis of molecular spectra can provide unique knowledge on the relativistic, many-body and quantum electrodynamics (QED) effects in the non-perturbative domain of high nuclear charges and super strong electromagnetic fields.

Theoretical understanding of the critical-field phenomena in heavy quasi-molecules requires, in general, solution of the two-center time-dependent Dirac equation. For low velocities of colliding ions this equation may still be treated adiabatically and, hence, can be traced back to the static (two-center) eigenproblem:

$$\hat{H}_{2C}\Psi = \epsilon\Psi, \quad (1)$$

where Ψ is the electronic wavefunction and the Hamiltonian \hat{H}_{2C} is given, for the simplest case of the one-electron-two-nuclei system, by:

$$\hat{H}_{2C} = \hat{H}_{free} + \hat{V}(\vec{r}, \vec{R}). \quad (2)$$

Here, \hat{H}_{free} is the free electron Dirac Hamiltonian and \hat{V} describes Coulomb interaction between an electron and two nuclei with $\vec{R} = \vec{R}_1 - \vec{R}_2$ being the inter-nuclear vector.

A large number of methods have been proposed during the last two decades for solving the eigenproblem (1) and, thus, for performing propagation of the electron wave packet in (slowly varying) nuclear potential. Most of these methods are based on the well-elaborated linear-combination-of-atomic-orbitals (LCAO) approach (Sepp et al. 1986, Toshima & Eichler 1988, Momberger et al. 1993, Rumrich et al. 1993, Eichler & Meyerhof 1995, Schulze et al. 1998, Gail et al. 2003, Tupitsyn et al. 2010). Within the LCAO approach, the (quasi-) molecular wavefunctions Ψ are constructed from two sets of atomic orbitals centered on two nuclei. Despite the relatively simple treatment of dimer quasi-molecules at large inter-nuclear distances, the LCAO method may encounter computational difficulties if ions are placed close to each other and the orbitals become much more molecular than atomic.

For rather small inter-nuclear distances, the two-center Dirac problem (1)–(2) can be solved efficiently in prolate spheroidal coordinates as discussed, for example, in

Ref. (Kullie & Kolb 2001). Unlike LCAO, the elliptic coordinates, being essentially two-center, are very practical for the accurate description of molecular terms. In contrast, they do not fit very well for the description of the “atomic-type” wavefunctions. Therefore, to the best of our knowledge, the application of the prolate spheroidal coordinates becomes less efficient with the increase of the distance between ions.

Besides the application of the elliptic coordinates, the structure and dynamics of heavy quasi-molecules at small inter-nuclear distances can be relatively well understood within the so-called monopole approximation (Müller-Nehler & Soff 1994, Ackad & Horbatsch 2008). Such an approximation, that employs solely the spherically symmetrical part of the two-center potential, allows one to reduce the problem to the spherically-symmetric one, with a total nuclear charge distributed homogeneously on the spherical shell with the diameter equal to the internuclear distance. This method was found to be very useful for description of strong-field phenomena in close ion collisions but, again, its accuracy is known to be poor when Dirac centers appear to be far from each other.

At the end of our brief review we should mention also the direct numerical integration of the two-center Dirac equation. Towards this line, the various lattice methods have been developed over the last decades (Becker et al. 1986, Strayer et al. 1990, Thiel et al. 1992, Momberger et al. 1996, Wells et al. 1996, Ionescu & Belkacem 1999, Busic et al. 2004, Şengül et al. 2009). Being potentially very precise these methods are, however, rather time-consuming, which puts restrictions on their broad application.

As seen from the discussion above, many of the methods available nowadays for solving the eigenproblem (1) and performing the time-propagation of electron (or positron) wave packets have restricted ranges of application. Moreover, the proper description of the positive- as well as the negative-continuum solutions of the (two-center) Dirac equation remains also a rather difficult task. In this contribution, we present an efficient theoretical approach for the treatment of the relativistic two-center problem at arbitrary inter-nuclear distance. Within this approach we employ the finite (discrete) basis solutions, as constructed in Cassini coordinates from the B-spline sets, in order to solve Eq. (1) and to find a (quasi) *complete* set of eigenvalues and eigenfunctions. On the basis of such a set that includes not only bound- but also (positive and negative) continuum-solutions of Eq. (1), further analysis can be performed both, for the quantum electrodynamics (QED) corrections to energy levels of heavy quasi-molecules and for the dynamical behavior of these molecules in (slow) ion-ion collisions.

The paper is organized as follows. In the next section we shall provide the detailed description of the method. In particular we will discuss the choice of the coordinates, describe the finite basis set approach and introduce the basis functions. The details of computations are given then in Sec. 3. In order to illustrate the application of the method, detailed calculations are performed for the energy spectra of H_2^+ , Th_2^{179+} and U_2^{183+} quasi-molecules. In Sec. 4 we will discuss the results of these calculations and will

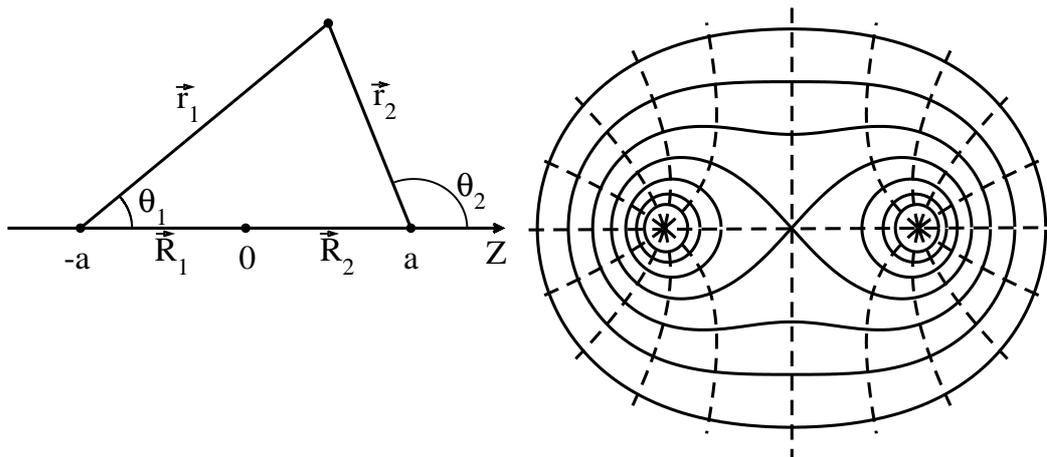


Figure 1. The explanation of the Cassini coordinates (left) and the lines with constant w and δ variables (right). On the right picture the solid lines are with constant value of w and the dashed ones - with constant δ .

compare them with the previously reported data. Finally, short summary and outlook will be given in Sec. 5.

The natural system of units ($c = m_e = \hbar = 1$; the energy unit is the electron rest mass $m_e c^2$) is used throughout the paper.

2. Theoretical background

2.1. Cassini coordinates

As mentioned already in the Introduction, the proper choice of the coordinate system may significantly simplify theoretical treatment of the two-center Dirac problem. In our analysis below, we shall solve the Dirac equation in the so-called Cassini coordinates. Since the properties of the Dirac equation in this orthogonal coordinate system have been investigated in Refs. (Schlüter et al. 1983, Wietschorke et al. 1983), here we may restrict ourselves to a rather short account of the basic relations. The Cassini coordinates w , δ , and ϕ of the electron relative to the nuclei are defined as follows:

$$w = \frac{\sqrt{r_1 r_2}}{a}, \quad (3)$$

$$\delta = \frac{\theta_1 + \theta_2}{2}, \quad (4)$$

$$\phi = \phi, \quad (5)$$

where r_i is the distance between the electron and the i -th nucleus and $a = |\vec{R}_1 - \vec{R}_2|/2$ is the half of internuclear distance (see Fig. 1). Moreover, the angle between the internuclear axis (Z -axis) and the position vector of the electron relative to the i -th nucleus is denoted as θ_i while, finally, ϕ is the azimuthal angle.

The Cassini coordinates introduced in Eqs. (3)–(5) are known to obey several important properties. For example, the curves corresponding to constant values of

the coordinate w form *closed* lines around the first ($0 < \delta < \pi/2$) or the second ($\pi/2 < \delta < \pi$) center if $w < 1$. In contrast, for the values of w greater than one, the (w -) equidistant curves surround both centers as it can be seen from the right panel of Fig. 1. Finally, the line $w = 1$ is lemniscate.

Another important feature of Cassini coordinates concerns the behavior of the (two-center) Coulomb potential along w -equidistant lines. For instance, as it has been shown in Ref. (Wietschorke et al. 1983) for the particular case of two point-like nuclei with charges $Z_1 = Z_2$, the electrostatic potential as calculated along the curve $w = \text{const}$ deviates from its mean value by less than 1.5 % for $w < 0.25$ and $w > 4$ and by about 17.2 % in the worst case of $w = 1$. Such a behavior selects out Cassini coordinates as the most adequate choice of coordinates for the solution of the two-center problem, since the curves $w = \text{const}$ almost coincide with the equipotential lines.

After having discussed the basic properties of Cassini coordinates, we shall employ them to re-write the Dirac Hamiltonian (2) in the form:

$$\hat{H}_{2C} = -i \frac{D^{1/4}}{aw} \left(\alpha_3 \frac{\partial}{\partial w} + \alpha_1 \frac{1}{w} \frac{\partial}{\partial \delta} \right) - i \alpha_2 \frac{1}{\rho} \frac{\partial}{\partial \phi} + V(w, \delta; a) + \beta m, \quad (6)$$

where α_i and β are the Dirac matrices and V is the two-center Coulomb potential. Explicit form of this potential depends on the particular choice of nuclear charge distribution and will be discussed later in Section 3. In Eq. (6) ρ is the distance between the electron and the internuclear axis:

$$\rho = \frac{a}{\sqrt{2}} \sqrt{\sqrt{D} - 1 - w^2 \cos 2\delta}, \quad (7)$$

and D is the discriminant

$$D = w^4 + 2w^2 \cos 2\delta + 1. \quad (8)$$

Because of the axial symmetry of the problem, it is convenient to seek the eigenfunctions of the Hamiltonian (6) in the form

$$\Psi(w, \delta, \phi) = \psi_\mu(w, \delta) \exp(i\mu\phi), \quad (9)$$

with $\mu = \pm 1/2, \pm 3/2, \pm 5/2, \dots$ being the projection of the total angular momentum of electron onto the internuclear axis. For such a choice of the total wavefunction, the Dirac Hamiltonian \hat{H}_{2C} reduces to

$$\hat{H}_{2C}^{(\mu)} = -i \frac{D^{1/4}}{aw} \left(\alpha_3 \frac{\partial}{\partial w} + \alpha_1 \frac{1}{w} \frac{\partial}{\partial \delta} \right) + \alpha_2 \frac{\mu}{\rho} + V(w, \delta; a) + \beta m, \quad (10)$$

and the problem becomes two-dimensional. The solution of this eigenproblem is, however, not a simple task owing to the fact that the Hamiltonian (10) is complex if the standard representation of Dirac matrices is used. It is often more convenient, therefore, to use an alternative representation in which matrices α_1 and α_3 are purely imaginary while α_2 is real. This can be easily achieved if one defines (new) Dirac matrices as (Schlüter et al. 1983):

$$\alpha_i = \gamma^0 \gamma^i, \quad (11)$$

where

$$\gamma^0 = \sigma_3 \otimes I, \quad (12)$$

$$\gamma^1 = i\sigma_2 \otimes \sigma_2, \quad (13)$$

$$\gamma^2 = i\sigma_2 \otimes \sigma_1, \quad (14)$$

$$\gamma^3 = -i\sigma_1 \otimes I, \quad (15)$$

with σ_i and I being the Pauli and unity matrices, correspondingly.

2.2. Finite basis set method

Equation (10) displays the reduced Dirac Hamiltonian that describes—in Cassini coordinates—the motion of a single electron in the field of two nuclei. So far, a few approaches have been proposed to find the eigenvalues and eigenfunctions of such a Hamiltonian. In Refs. (Schlüter et al. 1983, Wietschorke et al. 1983), for example, authors made use of the semi-discrete Galerkin method in order to solve the relativistic two-center eigenproblem. An alternative route can be developed based on the *finite basis set* method. Although both, the Galerkin and the finite-basis-set methods are variational ones, the latter approach seems to be preferable since it provides a (quasi-) *complete* set of eigenvectors. The knowledge of such a set is substantial for the theoretical analysis of the dynamical properties of heavy quasi-molecules. Moreover, the summation over the complete spectrum is required for the computation of the radiative corrections to the molecular energy levels. In this Section, therefore, we will briefly recall the main ideas of the finite basis set method and will discuss how this method is applied to find (a complete set of) eigenfunctions and eigenvalues of the Dirac Hamiltonian (10).

In order to construct the finite basis sets, we shall start from the principle of least action:

$$\delta S = 0, \quad (16)$$

from which the Dirac equation can be derived. In this expression, the action S is defined as:

$$S = \langle \psi_\mu | \hat{H}_{2C}^\mu - \varepsilon | \psi_\mu \rangle, \quad (17)$$

where ε is the Lagrange multiplier, introduced to ensure the normalization condition, which can be written in Cassini coordinates as

$$\langle \psi_\mu | \psi_\mu \rangle = \int dw d\delta \frac{aw}{D^{1/4}} \psi_\mu^\dagger \psi_\mu = 1. \quad (18)$$

Here, the wave function ψ_μ is the standard Dirac four-spinor, whose (four) components ψ_μ^i , $i = 1, \dots, 4$ we write as a *finite* expansion

$$\psi_\mu^{(i)}(w, \delta) = \sum_{\alpha=1}^N C_{\mu,\alpha}^{(i)} \mathcal{B}_\alpha(w, \delta), \quad (19)$$

over some basis functions $\mathcal{B}_\alpha(w, \delta)$. The explicit form of these functions is not crucial for the following discussion and will be specified later in Section 2.3. Mathematically,

the implication of Eq. (19) is equivalent to the projection of the whole space of wave functions ψ_μ onto the subspace, which basis is given by a set $\{\mathcal{B}_\alpha\}$.

By inserting now the wave function Eq. (19) into the least action principle (16) and by evaluating the variation δS with respect to change of expansion coefficients $C_{\mu,\alpha}^{(i)}$, we obtain the system of differential equations:

$$(\delta S)_j = \frac{\partial S}{\partial (\vec{C})_j} = 0, \quad (20)$$

where, for the sake of shortness, we use notation $(\vec{C})_j \equiv C_{\mu,\alpha}^{(i)}$. From this system immediately follows the matrix equation to determine the vector $\vec{C} = \{(\vec{C})_1, \dots, (\vec{C})_{4N}\}$:

$$A\vec{C} = \varepsilon K\vec{C}, \quad (21)$$

where A and K are $4N \times 4N$ matrices, constructed from $N \times N$ blocks:

$$A = \begin{pmatrix} (V + mB) & 0 & W & M - \Delta \\ 0 & (V + mB) & M + \Delta & W \\ -W & M - \Delta & (V - mB) & 0 \\ M + \Delta & -W & 0 & (V - mB) \end{pmatrix}, \quad (22)$$

$$K = \begin{pmatrix} B & 0 & 0 & 0 \\ 0 & B & 0 & 0 \\ 0 & 0 & B & 0 \\ 0 & 0 & 0 & B \end{pmatrix}. \quad (23)$$

Here, elements of the matrices B , V , M , W , and Δ are given in terms of the integrals involving the basis functions \mathcal{B}_i :

$$B_{i,k} = \int dw d\delta \frac{aw}{D^{1/4}} \mathcal{B}_i \mathcal{B}_k, \quad (24)$$

$$V_{i,k} = \int dw d\delta \frac{aw}{D^{1/4}} \mathcal{B}_i \mathcal{B}_k V(w, \delta), \quad (25)$$

$$M_{i,k} = \int dw d\delta \frac{aw}{D^{1/4}} \mathcal{B}_i \mathcal{B}_k \frac{\mu}{\rho}, \quad (26)$$

$$W_{i,k} = \int dw d\delta \mathcal{B}_i \frac{\partial \mathcal{B}_k}{\partial w}, \quad (27)$$

$$\Delta_{i,k} = \int dw d\delta \frac{\mathcal{B}_i}{w} \frac{\partial \mathcal{B}_k}{\partial \delta}. \quad (28)$$

Equation (21) is known as a generalized eigenvalue problem that can be solved by employing the standard techniques from linear algebra. In the present work, for example, we have used the well-established *Linear Algebra PACKage* Ref. (LAPACK 2008), which provides fast and effective routines for solving systems of linear equations.

2.3. Basis functions

By solving the generalized eigenvalue problem one obtains both, the energies ϵ_μ of the molecular levels and the (sets of) expansion coefficients $C_{\mu,\alpha}^{(i)}$. Thus, any theoretical analysis of the structure and dynamics of “one-electron-two-nucleus” system can be

traced back to the system of equations (21). As seen from Eqs. (22)–(28), however, in order to define such a system one has to agree first about the explicit form of the basis functions \mathcal{B}_α . In the present work we will construct these functions from the B-spline sets. During the last decades, the B-spline sets have been already successfully applied for the treatment of the one-center Dirac (Johnson et al. 1988, Froese Fischer & Parpia 1993) as well as the two-center Schrödinger problems (Artemyev et al. 2004). In these works it has been argued that the methods based on B-splines provide a quasi-complete set of solutions of the Dirac (or Schrödinger) equation, which allows perturbative calculations, implying summation over whole (or part) of the spectrum.

The properties of B-splines are described in details in Ref. (de Boor 1978). Here we like to recall briefly their main features that are crucial for an accurate solution of the Dirac problem. The B-splines of the k -th order are defined by the recurrence relation

$$B_i^k(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(x), \quad (29)$$

where the B-splines of the first order read as

$$B_i^1(x) = \begin{cases} 1, & t_i \leq x < t_{i+1} \\ 0, & \text{otherwise} \end{cases}. \quad (30)$$

In these expressions, the number of arbitrary positioned knots t_i is by k larger than the number of splines. Moreover, the first and the last k knots must be equal.

Before we discuss the construction of the basis functions \mathcal{B}_α , let us first recall the analytical properties of the B-splines. Namely, it follows from Eqs. (29)–(30) that: (i) B-splines of k -th order are piecewise polynomials of $(k - 1)$ order, (ii) the i -th B-spline of k -th order is defined on the interval from t_i to t_{i+k} , (iii) the splines together with their $(k - 1)$ derivatives are continuous, and (iv) the sum of all B-splines of given order at any point is equal to 1. These properties make the B-splines remarkably convenient for the numerical approximation of the basis functions from Eq. (19), which can be written as:

$$\mathcal{B}_\alpha = f(w, \delta) B_{l(\alpha)}^{n_w}(w) B_{m(\alpha)}^{n_\delta}(\delta). \quad (31)$$

Here $B_l^{n_w}(w)$ and $B_m^{n_\delta}(\delta)$ are two independent sets of B-splines. The function f has been chosen to describe the behavior of the Dirac wavefunction in regions, where the polynomial approximation fails. For an accurate treatment of two-center Dirac problem this function reads:

$$f(w, \delta) = \sqrt{\frac{\rho}{\sqrt{D}}}, \quad (32)$$

where ρ and D are given by Eqs. (7) and (8), correspondingly. Finally, for evaluation of Eq. (31) we have used equidistant knots for constructing the δ -splines and an exponential grid ($t_{i+1} = \lambda t_i$, $\lambda > 0$) for the w -splines.

After the description of the finite-basis-set approach we are ready now to discuss its numerical implication. In the following section, therefore, we shall present details of calculations leading to an accurate determination of energy spectrum and (a set of) eigenfunctions of heavy quasi-molecules.

3. Details of calculations

To solve the generalized eigenvalue problem (21) and, hence, to find energy values and functions of the two-center Dirac Hamiltonian, we first need to compute the matrix elements (24)–(28), which involve the basis functions \mathcal{B}_α . In the present work such a computation has been performed numerically by making use of the Gauss–Legendre quadratures. While the numerical integration can be performed rather easily in almost the entire space, it becomes a complicated task in the vicinity of the middle of the internuclear axis ($w = 1$, $\delta = \pi/2$). The power series expansion of the distance between an electron and internuclear axis ρ converges badly at this point leading to a lack of accuracy. However, noticing that \sqrt{D} is the generating function of the Gegenbauer polynomials (Erdélyi et al. 1953) and taking into account Eq. (7), there is the possibility for accurate evaluation of ρ by making use of expansions:

$$\rho = \begin{cases} \frac{aw^2}{\sqrt{2}} \sqrt{\sum_{n=0}^{\infty} C_{n+2}^{-1/2}(-\cos 2\delta) w^{2n}} & w < 1 \\ \frac{a}{\sqrt{2}} \sqrt{(w^2 - 1)(1 - \cos 2\delta) + w^2 \sum_{n=2}^{\infty} C_n^{-1/2}(-\cos 2\delta) w^{-2n}} & w > 1 \end{cases} \quad (33)$$

where $C_n^\lambda(x)$ are Gegenbauer polynomials defined by

$$C_0^\lambda(x) = 1, \quad (34)$$

$$C_1^\lambda(x) = 2\lambda x, \quad (35)$$

$$C_{(n+1)}^\lambda(x) = \frac{2(n + \lambda) x C_n^\lambda(x) - (n + 2\lambda - 1) C_{(n-1)}^\lambda(x)}{n + 1}. \quad (36)$$

Here we would like to point to a misprint in the expansion for ρ as given by Eq. (33) in Ref. (Wietschorke et al. 1983).

As seen from Eq. (25), apart from the basis functions \mathcal{B}_α , the knowledge on the two-center potential $V(w, \delta; a)$ is also required for the integration of the generalized eigenproblem. Explicit form of this operator, that enters the Dirac Hamiltonian (10), depends on the nuclear charge distribution employed. For example, the motion of the electron in the field of two point-like nuclei with the same charge number $Z_1 = Z_2 = Z$ is defined by the potential:

$$V(w, \delta; a) = -\alpha Z \frac{\sqrt{2}}{aw^2} \sqrt{\sqrt{D} + 1 + w^2}. \quad (37)$$

More complicated expression is required to account for the finite nuclear size effects or in the case of hetero-nuclear problem. To derive this, we should start from the general definition of two-center potential:

$$V = V_1(|\vec{r} - \vec{R}_1|) + V_2(|\vec{r} - \vec{R}_2|), \quad (38)$$

where V_i is the potential, generated by i -th nucleus. As usual in atomic structure calculations, such a single-center potential can be obtained as

$$V_i(r) = \int_{r_>} \frac{\rho_i(r_1)}{r_1^2} dr_1, \quad (39)$$

with ρ_i being the nuclear charge density distribution. By employing the various models of the charge distribution ρ_i one can explore the isotope effects on the structure and dynamics of heavy quasi-molecules. In the present work, for example, we shall use the well-known Fermi distribution:

$$\rho_i(r) = \frac{N}{1 + \exp[(r - c)/a]}, \quad (40)$$

where N is normalization factor and the parameters a and c can be expressed in terms of the nuclear root-mean square radius (see for example (Shabaev 1993)). Moreover, in Eqs. (38) and (39), the distance between the i -th nucleus and the electron is given in Cassini coordinates by:

$$|\vec{r} - \vec{R}_{1,2}| = \sqrt{(z \pm a)^2 + \rho^2} \quad (41)$$

$$z = \frac{a^2 w^2 \sin 2\delta}{2\rho}, \quad (42)$$

where the *plus* sign refers to $|\vec{r} - \vec{R}_1|$ and the *minus* sign to $|\vec{r} - \vec{R}_2|$.

4. Results and discussions

4.1. Spectra of heavy ions

Before starting the discussion on the predictions of the finite basis set approach for heavy quasi-molecules, let us first demonstrate the validity of the method if applied to much simpler, *one-center* Dirac problem. Reduction to such a (purely atomic) problem can be easily achieved if one takes one of the nuclear charges in Eq. (38) to be *zero*. The second nucleus with charge $Z \neq 0$ can be treated as point-like which bound-state energies given by a well-known expression:

$$\varepsilon = \left(1 + \frac{(\alpha Z)^2}{\left(\sqrt{(j + 1/2)^2 - (\alpha Z)^2} + n - j - 1/2 \right)^2} \right)^{-1/2}, \quad (43)$$

where n is the principal quantum number and j is the total momentum of electron. To perform an extensive check of our theoretical approach, detailed calculations of the energy values of hydrogen-like ions were carried out in the Cassini coordinates for various values of inter-center distance a from 10^{-4} to 20 a.u. and were compared against the predictions of Eq. (43). Special attention in these calculations has been paid to heavy nuclei with charge $92 \leq Z \leq 100$. For this high- Z regime and for relatively large ($a > 2$ a.u.) as well as small ($a < 5 \times 10^{-3}$) inter-center distances, we were able to reproduce the energies of the first 20 bound states with a relative accuracy of about 10^{-9} by employing in Eq. (31) only 40 w -splines of fifth order and 20 δ -splines of fourth order. In contrast, the number of B-splines had to be increased up to 45 and 28, respectively, in order to achieve a slightly worse accuracy of 10^{-7} for the intermediate region with $a \approx 10^{-2}$ a.u.,

While performing calculations for the energy values and eigenfunctions of the one-center Dirac Hamiltonian we were faced with the well known problem of *spurious states*,

i.e., non-physical solutions of Eq. (21). Being the general problem of the finite-basis-set methods applied to Dirac equation, the spurious states (as well as the ways for their elimination) have been discussed in the literature (Drake & Goldman 1981, Johnson et al. 1988, Shabaev et al. 2004, Igarashi 2006, Igarashi 2007). In Ref. (Shabaev et al. 2004), for example, authors have argued that application of the identical basis function sets for description of the large and small components of relativistic wavefunctions leads to the appearance of the non-physical solutions of the (one-center) Dirac-Coulomb problem. It has been also demonstrated, that one can get rid of these spurious states by using the so-called dual kinetically balanced basis (DKB) set constructed from functions that provide correct relation between the large and small components of the wavefunction in the non-relativistic limit. However, such a DKB approach is most efficient when applied to the spherically symmetric Dirac problem, which can be easily reduced to a one-dimensional radial equation and two-component wave function. In the case of a two-center potential, the construction of the kinetically balanced set is not a simple task. The studies towards the extensions of DKB method to the two-center Dirac problem are currently underway and will be presented elsewhere.

Apart from applying the DKB approach, one can eliminate the spurious, non-physical solutions of Eq. (21) if analyzes their oscillatory behavior. Namely, the spurious eigenfunctions with energies in the range $-mc^2 < \epsilon < +mc^2$ differ from the physical *bound* solutions by significantly faster oscillations. Since all the basis functions (31) are positive-defined, the only possibility for the function (19) to oscillate fast, is to have alternating-sign coefficients. Therefore, for bound state solutions one can easily determine the spurious states by evaluating the value

$$S_\mu^i = \sum_{\alpha: \delta < \pi/2; C_{\mu,\alpha}^{(i)} \neq 0} \frac{|C_{\mu,\alpha}^{(i)}|}{C_{\mu,\alpha}^{(i)}}, \quad (44)$$

where the summation runs over all non-zero expansion coefficients $C_{\mu,\alpha}^{(i)}$ from Eq. (19), corresponding to basis functions defined at $\delta < \pi/2\ddagger$. For basis sets constructed from 800 to 2500 functions the (absolute value of) coefficient S_μ^i was found to be less than 15 if $\psi_\mu^{(i)}$ is spurious state and greater than 100 for the physical solutions.

4.2. Quasi-molecular spectra

So far, we have discussed the application of the finite basis set approach to the one-center Dirac problem. Calculations carried out for such an ‘‘atomic scenario’’ were used by us for estimating the inherent inaccuracies, associated with the method. Now we are ready to perform the detailed analysis of the energy spectra of (quasi-) molecules.

Up to date, several attempts have been made to solve the two-center Dirac equation and to determine the binding energies of homonuclear dimers. See e.g. (Schulze et al. 1998, Kullie & Kolb 2001, Tupitsyn et al. 2010). In Ref. (Kullie & Kolb 2001), for

\ddagger The summation over the entire space ($0 < \delta < \pi$) in Eq. (44) in homonuclear case will lead to vanishing of S_μ^i also for all physical states, which are odd with respect to the change $\delta \rightarrow \pi - \delta$.

Table 1. Binding energy of $1\sigma_g$ quasi-molecular state in atomic units.

System	H_2^+ , $R=2$ a.u.	Th_2^{179+} , $R=2/90$ a.u.	U_2^{183+} , $R=2/92$ a.u.
This work, point-like nucleus	-1.1026409	-9504.752	-9965.375
Others, point-like nucleus	-1.1026416 ^a	-9504.757 ^a	-9965.307 ^b
This work, finite-size nucleus	-1.1026401	-9498.448	-9957.796

^a Ref. (Kullie & Kolb 2001)^b Ref. (Tupitsyn et al. 2010)

example, accurate data were reported for the values of the $1\sigma_g$ ground state energy of the H_2^+ and Th_2^{179+} molecules. The calculations have been done at the “chemical” internuclear distance of $R = 2/Z$ a.u. and by employing the point-like nuclear charge distributions. Predictions, obtained in Ref. (Kullie & Kolb 2001) for such a model case, are presented in Table 1 and are compared with the solutions of the generalized eigenvalue problem (21) for the “point-like” potential (37). As seen from the table, the ground-state energies of both molecules are well reproduced (up to 7 decimal digits) within the final basis set approach. Apart from the H_2^+ and Th_2^{179+} dimers, we have also explored the spectrum of the U_2^{183+} molecule. Perfect agreement between our prediction and data reported recently in Ref. (Tupitsyn et al. 2010) has been again found for the energy $\epsilon_{1\sigma_g}$ (see right column of Table 1).

While over the past decades the spectra of heavy quasi-molecules have been studied rather intensively for the *point-like* nuclei, not much is known about the nuclear-size corrections to the molecular levels. In order to estimate these corrections we made use of Eqs. (38)–(40) with the proper values of root-mean square radii from (Angeli 2004, Kozhedub et al. 2008) and evaluated the ground-state energies of the H_2^+ , Th_2^{179+} and U_2^{183+} dimers. As can be expected, we found that while for low- Z molecules the effect of finite nuclear size is almost negligible, it becomes sizable in the high- Z domain. For example, as seen from Table 1, the absolute value of the $\epsilon_{1\sigma_g}$ binding energy of U_2^{183+} quasi-molecule reduces by about 206 eV (7.5 a.u.) if Fermi-type nuclear charge distribution is taken into account.

Up to here, we have discussed the (quasi-) molecular energies as well as the nuclear-size effects for a single inter-nuclear distance $R = 2/Z$ a.u. In future experiments, however, formation of heavy quasi-molecules is to be observed in (slow) collisions of high- Z ions, the distance between which will vary with time: $R = R(t)$. To understand better the R -dependence of the molecular spectra, detailed calculations for the energies of the ground $1\sigma_g$ and the first excited $1\sigma_u$ states of the U_2^{183+} dimer have been performed for a wide range of internuclear distances. Results of these calculations are presented in Fig. 2 for both, point-like (dashed line) and extended (solid line) nuclei. Moreover, we plot also the energy of the $1s$ state, calculated in monopole approximation (dash-dotted line) which corresponds to the solution of the Dirac equation with the spherically symmetric part of the two-center potential. As seen from the figure, the $1\sigma_g$ and $1\sigma_u$ binding energies tend—for the large inter-nuclear distances—to the energy of the

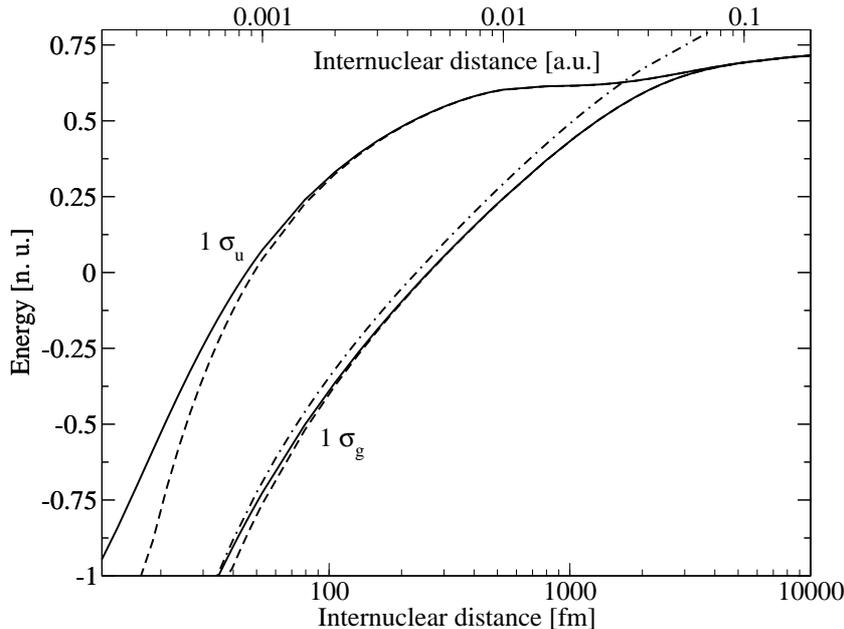


Figure 2. The energy of 1σ states in U_2^{183+} as a function of internuclear distance. The solid and dashed lines correspond to finite-size and point-like nuclei, respectively. The dash-dotted line represents the energy of the $1s$ state in spherically-symmetrical mono-pole approximation, centered in the middle point of inter-nuclear axis.

$1s$ ground state of hydrogen-like uranium U^{91+} . Such a well-understood behavior of molecular terms is not reproduced, however, by the monopole approximation for which the energy approaches the value of $\epsilon = mc^2$ if $R \rightarrow \infty$. As the nuclei come closer to each other, the difference between the energy of even (also known as “gerade”) and odd (“ungerade”) symmetry states becomes noticeable. Again, this splitting is well described by our two-center Dirac calculations but can not be obtained within the (spherical) monopole model. Finally, at the very small, so-called *critical*, internuclear distances the energy levels of U_2^{183+} quasi-molecule “dive” into the Dirac negative continuum, leading to an instability of the physical vacuum against electron-positron pair production.

By inspecting Fig. 2 and Table 2 one can see that the finite-nuclear size correction to the energy levels of U_2^{183+} varies significantly with the distance between the nuclei. For the ground, $1\sigma_g$, state, for example, this correction does not exceed 0.1% of the total energy at the “chemical” inter-nuclear distance $R = 2/92$ a.u. (see also right column of Table 1) but increases to almost 10% if $R \approx 40$ fm. Even larger effect can be observed at this distance for the first excited state for which the absolute value of the binding energy $\epsilon_{1\sigma_u}$ reduces by almost factor of two if one accounts for the finite nuclear size effects (see Table 2). These corrections to the energy levels of heavy quasi-molecule result, of course, in a significant dependence of the critical radius R_{crit} , i.e., of the distance at which these levels “dive” into the negative continuum, on the nuclear charge distribution. For the ground state, for example, our finite-basis-set calculations suggest that the R_{crit} decreases from 38.4 fm for the point-like to 34.7 fm for the finite-

Table 2. $1\sigma_g$ and $1\sigma_u$ energies in natural units as functions of internuclear distance R .

$R[\text{fm}]$	$\epsilon_{1\sigma_g}$ Point nucleus	$\epsilon_{1\sigma_u}$ Point nucleus	$\epsilon_{1\sigma_g}$ Finite nucleus	$\epsilon_{1\sigma_u}$ Finite nucleus	ϵ_{1s} Mono-pole
26.46	Neg. cont.	-0.46415	Neg. cont.	-0.32584	Neg. cont.
38.5	-0.99842	-0.14956	-0.92831	-0.08908	-0.90882
52.92	-0.76208	0.04524	-0.72506	0.07514	-0.68872
264.59	0.00632	0.52711	0.00851	0.52835	0.05200
529.18	0.24414	0.60211	0.24499	0.60280	0.29291
2645.89	0.63382	0.65132	0.63418	0.65174	0.73055
5291.77	0.69193	0.69219	0.69231	0.69258	0.84359
26458.86	0.73134	0.73134	0.73172	0.73173	0.96572
52917.72	0.73623	0.73624	0.73662	0.73662	0.98531

size nuclei. These estimates were found to be in a perfect agreement with the previous calculations by Tupitsyn and co-workers who reported values of 38.43 fm and 34.72 fm, correspondingly (Tupitsyn et al. 2010). Moreover, our data are in accordance with the value $R_{\text{crit}} = 35$ fm obtained in Ref. (Soff, Reinhardt & Betz 1978) within the monopole approximation.

In contrast to the $1\sigma_g$ ground state for which the finite-size effects just lead to a reduction of the critical radius R_{crit} , they prevent completely the excited $1\sigma_u$ orbital from the “diving” into the negative continuum before the collision of nuclei. This can be seen from Fig. 2 whose left border indicates the nuclear diameter of Uranium. At this distance, the binding energy $\epsilon_{1\sigma_u} = -0.947109$ n.u. is still far from the negative continuum threshold.

5. Summary and outlook

In summary, we have elaborated a finite-basis-set approach to deal with the two-center Dirac problem. Being constructed in Cassini coordinates, the basis functions allow one to solve the generalized eigenvalue equation (21) for all the range of inter-nuclear distances and to find a (quasi) complete set of eigensolutions. In order to illustrate the application of the method and to verify its accuracy, detailed calculations have been performed for the binding energies of H_2^+ , Th_2^{179+} and U_2^{183+} dimers. Special attention in these calculations has been paid to the finite nuclear corrections that were found to be of a paramount importance for an accurate description of molecular spectra especially at small distances between the nuclei. For the U_2^{183+} quasi-molecule, for example, these corrections not only reduce (the absolute value of) the ground-state energy by about 10 % but also prevent the first excited level $1\sigma_u$ from reaching the Dirac negative continuum.

The finite-basis-set method, yielding a *complete* set of eigenvalues and eigenfunctions of the two-center Dirac Hamiltonian, provide a powerful tool for studying

the dynamics of (slow) ion collisions including the electron–positron pair production. Moreover, it can be efficiently used for an accurate evaluation of radiative (QED) corrections to molecular energy levels, that requires the summation over the complete spectrum. Theoretical investigations towards these two lines are currently underway.

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References

- Ackad E & Horbatsch M 2008 *Phys. Rev. A* **78**, 062711.
- Angeli I 2004 *At. Data Nucl. Data Tables* **87**, 185 – 206.
- Artemyev A N, Ludeña E V, Karasiev V V & Hernández A J 2004 *Journal of Computational Chemistry* **25**, 368 – 374.
- Becker U, Grün N, Scheid W & Soff G 1986 *Phys. Rev. Lett.* **56**, 2016–2019.
- Betz W, Soff G, Müller B & Greiner W 1976 *Phys. Rev. Lett.* **37**, 1046–1049.
- Busic O, Grün N & Scheid W 2004 *Phys. Rev. A* **70**, 062707.
- de Boor C 1978 *A practical guide to splines* Springer New York.
- Drake G W F & Goldman S P 1981 *Phys. Rev. A* **23**, 2093–2098.
- Eichler J & Meyerhof W 1995 *Relativistic Atomic Collisions* Academic Press San Diego.
- Erdélyi A, Magnus W, Oberhettinger F & Tricomi F G 1953 *Higher transcendental functions* Vol. 2 McGraw-Hill New York.
- FAIR: *Conceptual Design Report: An International Accelerator Facility for Beams of Ions and Antiprotons* (edited by Henning W) 2001 GSI.
- Froese Fischer C & Parpia F A 1993 *Phys. Lett.* **A179**, 198 – 204.
- Gail M, Grün N & Scheid W 2003 *Journal of Physics B: Atomic, Molecular and Optical Physics* **36**, 1397.
- Gumberidze A, Bosch F, Bräuning-Demian A, Hagmann S, Kühl Th, Liesen D, Schuch R & Stöhlker Th 2005 *Nucl. Instr. Meth. B* **233**, 28–30.
- Gumberidze A, Stöhlker Th, Beyer H F, Bosch F, Bräuning-Demian A, Hagmann S, Kozhuharov C, Kühl Th, Mann R, Indelicato P, Quint W, Schuch R & Warczak A 2009 *Nucl. Instr. Meth. B* **267**, 248–250.
- Igarashi A 2006 *Journal of the Physical Society of Japan* **75**, 114301–1 – 114301–8.
- Igarashi A 2007 *Journal of the Physical Society of Japan* **76**, 054301–1 – 054301–6.
- Ionescu D C & Belkacem A 1999 *Physica Scripta* **T80**, 128 – 132.
- Johnson W R, Blundell S A & Sapirstein J 1988 *Phys. Rev. A* **37**, 307 – 315.
- Kirsch J, Betz W, Reinhardt J, Soff G, Müller B & Greiner W 1978 *Physics Letters B* **72**, 298 – 302.
- Kozhedub Y S, Andreev O V, Shabaev V M, Tupitsyn I I, Brandau C, Kozhuharov C, Plumien G & Stöhlker T 2008 *Phys. Rev. A* **77**, 032501.
- Kullie O & Kolb D 2001 *Eur. Phys. J. D* **17**, 167 – 173.

- LAPACK “*Linear Algebra PACKage – LAPACK*” (<http://www.netlib.org/lapack/>) Copyright (c) 1992–2008 The University of Tennessee.
- Momberger K, Belkacem A & Sørensen A H 1996 *Phys. Rev. A* **53**, 1605–1622.
- Momberger K, Grün N & Scheid W 1993 *Journal of Physics B: Atomic, Molecular and Optical Physics* **26**, 1851.
- Müller B 1976 *ARNS* **26**, 351 – 383.
- Müller-Nehler U & Soff G 1994 *Physics Reports* **246**, 101 – 250.
- Müller U, Soff G, de Reus T, Reinhardt J, Müller B & Greiner W 1983 *Z. Phys. A* **313**, 263–279.
- Rafelski J, Fulcher L P & Klein A 1978 *Physics Reports* **38**, 227 – 361.
- Reinhardt J, Müller B, Greiner W & Soff G 1979 *Phys. Rev. Lett.* **43**, 1307–1310.
- Rumrich K, Soff G & Greiner W 1993 *Phys. Rev. A* **47**, 215–228.
- Schlüter P, Wietschorke K H & Greiner W 1983 *J. Phys. A* **16**, 1999 – 2016.
- Schulze K, Anton J, Sepp W D & Fricke B 1998 *Phys. Rev. A* **58**, 1578–1580.
- Şengül M Y, Güçlü M C & Fritzsche S 2009 *Phys. Rev. A* **80**, 042711.
- Sepp W D, Kolb D, Sengler W, Hartung H & Fricke B 1986 *Phys. Rev. A* **33**, 3679–3687.
- Shabaev V M 1993 *J. Phys. B* **26**, 1103–1108.
- Shabaev V M, Tupitsyn I I, Yerokhin V A, Plumien G & Soff G 2004 *Phys. Rev. Lett.* **93**, 130405.
- Soff G, Greiner W, Betz W & Müller B 1979 *Phys. Rev. A* **20**, 169–193.
- Soff G, Müller B & Greiner W 1978 *Phys. Rev. Lett.* **40**, 540–544.
- Soff G, Reinhardt J & Betz W 1978 *Physica Scripta* **17**, 417.
- Soff G, Reinhardt J, Müller B & Greiner W 1977 *Phys. Rev. Lett.* **38**, 592–595.
- Soff G, Schlüter P, Reinhardt J, de Reus T, Wietschorke K H, Schäfer A, Graf S, Müller U, Müller B & Greiner W 1987 *Physica Scripta* **36**, 743.
- Stöhlker Th, Beyer H F, Bräuning H, Bräuning-Demian A, Brandau C, Hagmann S, Kozhuharov C, Kluge H J, Kühl Th, Liesen D, Mann R, Nörtershäuser W, Quint W, Schramm U, & Schuch R 2007 *Nucl. Instr. Meth. B* **261**, 234–238.
- Strayer M R, Bottcher C, Oberacker V E & Umar A S 1990 *Phys. Rev. A* **41**, 1399–1407.
- Thiel J, Bunker A, Momberger K, Grün N & Scheid W 1992 *Phys. Rev. A* **46**, 2607–2612.
- Toshima N & Eichler J 1988 *Phys. Rev. A* **38**, 2305 – 2316.
- Tupitsyn I I, Kozhedub Y S, Shabaev V M, Deyneka G B, Hagmann S, Kozhuharov C, Plumien G & Stöhlker T 2010 *arXiv:10045131v1 [physics:atom-ph]* .
- Verma P, Mokler P H, Bräuning-Demian A, Bräuning H, Berdermann E, Chatterjee S, Gumberidze A, Hagmann S, Kozhuharov C, Orsic-Muthig A, Reuschl R, Schöffner M, Spillmann U, Stöhlker Th, Stachura Z, Tashenov S & Wahab M A 2005 *Nucl. Instr. Meth. B* **235**, 309–314.
- Verma P, Mokler P H, Bräuning-Demian A, Kozhuharov C, Bräuning H, Bosch F, Liesen D, Stöhlker Th, Hagmann S, Chatterjee S, Gumberidze A, Reuschl R, Schöffner M, Spillmann U, Orsic-Muthig A, Tashenov S, Stachura Z & Wahab M A 2006 *Radiation Physics and Chemistry* **75**, 2014–2018.
- Wells J C, Oberacker V E, Strayer M R & Umar A S 1996 *Phys. Rev. A* **53**, 1498–1504.
- Wietschorke K H, Schlüter P & Greiner W 1983 *J. Phys. A* **16**, 2017 – 2034.