



# Relativistic calculations of the ground state energies and the critical distances for one-electron homonuclear quasi-molecules



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## ABSTRACT

The ground-state energies of one-electron homonuclear quasi-molecules for the nuclear charge number in the range  $Z = 1 - 100$  at the “chemical” distances  $R = 2/Z$  (in a.u.) are calculated. The calculations are performed for both point- and extended-charge nucleus cases using the Dirac-Fock-Sturm approach with the basis functions constructed from the one-center Dirac-Sturm orbitals. The critical distances  $R_{cr}$ , at which the ground-state level reaches the edge of the negative-energy Dirac continuum, are calculated for homonuclear quasi-molecules in the range:  $85 \leq Z \leq 100$ . It is found that in case of  $U_2^{183+}$  the critical distance  $R_{cr} = 38.42$  fm for the point-charge nuclei and  $R_{cr} = 34.72$  fm for extended nuclei.

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## 1. Introduction

A one-electron diatomic quasi-molecule represents the simplest molecular system. Precise calculations of one-electron homonuclear quasi-molecules are generally used for tests of various theoretical methods developed for calculations of diatomic systems. Theoretical analysis of the electronic structure of a one-electron quasi-molecular system consists in solving the one-electron two-center Schrödinger or Dirac equation.

In the nonrelativistic case the three-dimensional two-center Schrödinger equation can be transformed into two ordinary (one-dimensional) differential equations [1] and, therefore, can be solved to a high accuracy [2]. Moreover, the scaling  $r' = r/Z$  allows one to reduce the solution of the Schrödinger equation with the internuclear distance  $R$  and the nuclear charge  $Z$  to the solution of the same equation for the molecular ion  $H_2^+$  with the internuclear distance  $R/Z$ . This makes the molecular ion  $H_2^+$  to be a good test system for various theoretical methods. In the relativistic case, however, the variables can not be completely separated and the simple scaling is no longer valid. To date, various theoretical methods were developed to calculate homonuclear quasi-molecules [3–10]. Systematic calculations of the ground-states energies of molecular ions for a wide range of  $Z$  at the distances  $R = 2/Z$  were performed in Ref. [11].

Investigations of quasi-molecules formed during low-energy heavy-ion collisions with the total nuclear charge larger than the critical value,  $Z_1 + Z_2 \geq Z_{cr} \approx 172$ , can provide a unique possibility to study quantum electrodynamics (QED) at supercritical electromagnetic fields [12,13]. It is known that the ground-state level reaches the edge of the negative-energy spectrum, when the internuclear distance  $R$  becomes equal to the critical value  $R_{cr}$ . For the distances  $R < R_{cr}$ , the ground-state level dives into negative-energy Dirac continuum as a resonance. The critical distances  $R_{cr}$  were calculated for the point-charge nuclei in Refs. [14–16] and for extended nuclei in Refs. [17–19]. However, since the first calculations for extended nuclei were accomplished using either a crude numerical approach [17] or an approximate analytical method [18,19], their accuracy was rather low. In case of  $U_2^{183+}$ , the most precise calculations of the critical distance were performed in Refs. [20,21].

In the present work, high-precision relativistic calculations of the ground-state energies of molecular ions with the nuclear charges in the range  $Z = 1 - 100$  at “chemical distances”  $R = 2/Z$  (in a.u.) are performed. We also calculate the critical distances  $> R_{cr}$  for one-electron quasi-molecules in the range:  $85 \leq Z \leq 100$ . All the calculations, being performed for both point- and extended-charge nuclei, are based on the Dirac-Fock-Sturm method [22–24,20,25]. The basic equations of this method for the one-electron two-center problem are given in Section 2. In Section 3, we present the numerical results and compare them with the calculations performed by other methods.

Atomic units are used throughout the paper ( $\hbar = m = e = 1$ ).

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## 2. Dirac–Sturm method for the two-center problem

In the framework of the Born–Oppenheimer approximation the electronic wave function  $\psi(\vec{r})$  is determined by the Dirac equation:

$$\hat{h}_D \psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r}), \quad (1)$$

where  $\varepsilon_n$  is the energy of the stationary state and  $\hat{h}_D$  is the two-center Dirac Hamiltonian defined by

$$\hat{h}_D = c(\vec{\alpha} \cdot \vec{p}) + \beta c^2 + V_{AB}(\vec{r}). \quad (2)$$

Here  $c$  is the speed of light,  $\vec{\alpha}, \beta$  are the Dirac matrices,  $V_{AB}(\vec{r})$  is the two-center Coulomb potential,

$$V_{AB}(\vec{r}) = V_{\text{nucl}}^A(\vec{r}_A) + V_{\text{nucl}}^B(\vec{r}_B), \quad \vec{r}_A = \vec{r} - \vec{R}_A, \quad \vec{r}_B = \vec{r} - \vec{R}_B \quad (3)$$

and  $\vec{R}_A$  and  $\vec{R}_B$  determine the positions of the nuclei. The one-center Coulomb potential:

$$V_{\text{nucl}}(\vec{r}) = \begin{cases} -Z/r & \text{for the point-charge nucleus,} \\ -\int d\vec{r}' \frac{Z\rho_{\text{nucl}}(\vec{r}')}{|\vec{r}-\vec{r}'|} & \text{for the extended nucleus,} \end{cases} \quad (4)$$

where the nuclear charge density  $\rho_{\text{nucl}}(\vec{r})$  is normalized to unity ( $\int d\vec{r} \rho_{\text{nucl}}(\vec{r}) = 1$ ).

The two-center expansion of the stationary wave function  $\psi_n(\vec{r})$  is given by

$$\psi_n(\vec{r}) = \sum_{\alpha=A,B} \sum_a c_{\alpha a}^n \varphi_{\alpha a}(\vec{r} - \vec{R}_\alpha), \quad (5)$$

where index  $\alpha = A, B$  labels the centers and index  $a$  numerates the basis functions at the given center. The coefficients  $c_{\alpha a}^n$  of the expansion (5) can be obtained solving the generalized eigenvalue problem:

$$\sum_k H_{jk} c_k^n = \varepsilon_n \sum_k S_{jk} c_k^n, \quad (6)$$

where subscripts  $j$  and  $k$  numerate the basis functions of both centers, and the matrix elements  $H_{jk}$  and  $S_{jk}$  are given by

$$H_{jk} = \langle j | \hat{h}_D | k \rangle, \quad S_{jk} = \langle j | k \rangle. \quad (7)$$

As the basic functions, we consider the central-field bispinors centered at the positions of the ions:

$$\varphi_{n\kappa m}(\vec{r}) = \begin{pmatrix} \frac{P_{n\kappa}(r)}{r} \chi_{\kappa m}(\Omega, \sigma) \\ i \frac{Q_{n\kappa}(r)}{r} \chi_{-\kappa m}(\Omega, \sigma) \end{pmatrix}, \quad (8)$$

where  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  are the large and small radial components, respectively, and  $\kappa = (-1)^{l+j+1/2}(j+1/2)$  is the relativistic angular quantum number. The radial components are numerical solutions of the radial Dirac–Sturm equations in the central field potential  $V(r)$ :

$$\begin{aligned} c\left(-\frac{d}{dr} + \frac{\kappa}{r}\right) \overline{Q}_{n\kappa}(r) + (V(r) + c^2 - \varepsilon_{n_0\kappa}) \overline{P}_{n\kappa}(r) &= \lambda_{n\kappa} W_\kappa(r) \overline{P}_{n\kappa}(r), \\ c\left(\frac{d}{dr} + \frac{\kappa}{r}\right) \overline{P}_{n\kappa}(r) + (V(r) - c^2 - \varepsilon_{n_0\kappa}) \overline{Q}_{n\kappa}(r) &= \lambda_{n\kappa} W_\kappa(r) \overline{Q}_{n\kappa}(r). \end{aligned} \quad (9)$$

Here  $\lambda_{n\kappa}$  can be considered as an eigenvalue of the Dirac–Sturm operator and  $W_\kappa(r)$  is a constant sign weight function. In our calculations we use the following weight function:

$$W_\kappa(r) = -\frac{1 - \exp(-(\alpha_\kappa r)^2)}{(\alpha_\kappa r)^2}. \quad (10)$$

In contrast to  $1/r$ , this weight function is regular at the origin. The Sturmian operator is Hermitian and does not contain any continuum spectra. Therefore, the generalized eigenvalue equation with the weight function (10) yields a complete and discrete set of eigenfunctions that are orthogonal to each other with the weight (10).

Eq. (9) are solved using the finite difference method with a constant step on Brattsev's grid  $\rho = \alpha r + \beta \ln(r)$  [22]. These solutions, which have the right asymptotic behavior at the origin and infinity, are used to construct the basis set. In particular, for the two Coulomb point-charge centers the behavior of the basic functions at the origin is characterized by the fractional degree of the radius,  $\sim r^\gamma$  with  $\gamma = \sqrt{\kappa^2 - (Z/c)^2}$ .

The central-field potential  $V(r)$  in Eq. (9) can be chosen to provide the most appropriate basis. For instance, at small internuclear distances the potential  $V(r)$  at the center  $A$ , in addition to the Coulomb potential of the nucleus  $A$ ,  $V_{\text{nucl}}^A(r)$ , should also include the monopole part of the reexpansion of the potential  $V_{\text{nucl}}^B(\vec{r} - \vec{R}_B)$  with respect to the center  $A$ :

$$V^A(r) = V_{\text{nucl}}^A(r) + V_{\text{mon}}^B(r), \quad (11)$$

where

$$V_{\text{mon}}^B(r) = \frac{1}{4\pi} \int d\Omega_A V_{\text{nucl}}^B(\vec{r} - \vec{R}_B). \quad (12)$$

However, for the “chemical” distances ( $R = 2/Z$ ) taking into account the monopole potential of the second ion in Eq. (11) does not improve the convergence of the results with respect to the number of the basis functions. For this reason, we keep this term evaluating the critical distances and neglect it in the calculations at the “chemical” distances.

## 3. Results and discussion

High-precision relativistic calculations of the  $1\sigma_g$  state energy of one-electron homonuclear quasi-molecules at the distance  $R = 2/Z$  (in a.u.) have been performed employing the Dirac–Sturm method. The results of these calculations for the point- and extended-charge nuclei are given in Table 1. The extended-nucleus results were obtained using the Fermi model of the nuclear charge distribution:

$$\rho_{\text{nucl}}(r) = \frac{N}{1 + \exp[(r - r_0)/a]}, \quad (13)$$

where the parameter  $a$  was chosen to be  $a = 2.3/(4 \ln 3)$  and the parameters  $N$  and  $r_0$  are obtained using the values of the root-mean-square (rms) nuclear charge radii  $\langle r_n^2 \rangle^{1/2}$  taken from Refs. [26,27]. The point-nucleus results were recently presented in Ref. [28]. In these calculations we used the speed of light as obtained from the fine structure constant  $\alpha = 1/c$  (the value of  $\alpha$  is taken from CODATA [29]).

**Table 1**

Relativistic energies (a.u.) of the  $1\sigma_g$  quasi-molecular state for the point- and extended-charge nuclei and  $R = 2/Z$  a.u. (speed of light  $c = 137.035999074$  [29]).

Z	Ion	$\varepsilon_{1\sigma_g}$ (point-charge nucl.)	$\varepsilon_{1\sigma_g}$ (extended-charge nucl.)
1	H <sub>2</sub> <sup>+</sup>	-1.102641581032	
2	He <sub>2</sub> <sup>3+</sup>	-4.410654728260	-4.410654714140
10	Ne <sub>2</sub> <sup>19+</sup>	-110.3372043998	-110.3371741499
20	Ca <sub>2</sub> <sup>39+</sup>	-442.2399970985	-442.2392996469
30	Zn <sub>2</sub> <sup>59+</sup>	-998.4267621737	-998.4214646525
40	Zr <sub>2</sub> <sup>79+</sup>	-1783.587352661	-1783.563450815
50	Sr <sub>2</sub> <sup>99+</sup>	-2804.659800901	-2804.571434254
60	Nd <sub>2</sub> <sup>119+</sup>	-4071.309814908	-4071.036267926
70	Yb <sub>2</sub> <sup>139+</sup>	-5596.754834761	-5595.926978290
80	Hg <sub>2</sub> <sup>159+</sup>	-7399.228750561	-7397.028800116
90	Th <sub>2</sub> <sup>179+</sup>	-9504.756648531	-9498.588788490
92	U <sub>2</sub> <sup>183+</sup>	-9965.365357898	-9957.775519122
100	Fm <sub>2</sub> <sup>199+</sup>	-11952.94176701	-11936.41770218

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