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Solution of the Dirac equation using the Rayleigh-Ritz method: Flexible basis coupling large and small components. Results for one-electron systems

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An algebraic solution of the Dirac equation is reinvestigated. Slater-type spinor orbitals and their corresponding system of differential equations are defined in two- and four-component formalism. They describe the radial function in components of the wave function of the Dirac equation solution to high accuracy. They constitute the matrix elements arising in a generalized eigenvalue equation. These terms are evaluated through prolate spheroidal coordinates. The corresponding integrals are calculated by the numerical global-adaptive method taking into account the Gauss-Kronrod numerical integration extension. Sample calculations are performed using flexible basis sets generated with both signs of the relativistic angular momentum quantum number κ. Applications to one-electron atoms and diatomics are detailed. Variationally optimum values for orbital parameters are obtained at given nuclear separation. Methods discussed in this work are capable of yielding highly accurate relativistic two-center integrals for all ranges of orbital parameters. This work provides an efficient way to overcome the problems that arise in relativistic calculations.

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I. INTRODUCTION

The Dirac equation for quantum mechanical characterization of an electron moving through the Coulomb potential around a fixed-point-like nucleus of charge Ze, where e is the proton charge and Z is the atomic number, is written [1] as

$$\hat{H}_D \Psi = E\Psi, \tag{1}$$

where

$$\hat{H}_D = c(\vec{\alpha}\cdot\hat{\vec{p}}) + m_0c^2\beta - \frac{Ze^2}{r} \tag{2}$$

is the one-electron Dirac operator [in atomic units (a.u.); $\hbar = 1, m_0 = 1$, and $e^2/4\pi\epsilon_0 = 1$],

$$\Psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \tag{3}$$

is the two-component form of four-component electron spinor wave functions,

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{4}$$

c is speed of light, $\vec{\sigma}$ are Pauli spin matrices, $\hat{\vec{p}}$ is the momentum operator, m_0 is the electron rest mass, I is the 2×2 unit matrix, and ψ^L,ψ^S represent large and small components of the electron wave function with labels L,S which are used to denote the terms "large" and "small," respectively [2].

The spectrum obtained by the exact solution of the Dirac equation for one-electron atoms (i.e., it is known only for limited interactions with strong constraint on the potential [3,4]) does not have a finite lower bound, and it comprises three distinct intervals: the spectrum $(-\infty, -m_0c^2)$ that corresponds to the negative energy continuum states (referred to as the negative energy spectrum), the spectrum $(-m_0c^2, m_0c^2)$ that contains the discrete spectrum of bound states, and the spectrum (m_0c^2, ∞) that corresponds to positive continuum states (referred to as the positive energy spectrum). Note that in a Coulomb potential due to a positive charge, the bound states are part of the positive energy state spectrum because they can be related to the presence of electrons. The terminology used in Eq. (3) is preferred for the positive energy solutions, which correspond to electronic solutions. The lower components go to zero in the nonrelativistic limit and the upper components thus become a solution of the corresponding nonrelativistic equation, i.e., the Schrödinger equation.

Conversely, the algebraic solution of Dirac's equation is free from constraints on the potential but suffers from *variational collapse* [5,6], implying the possible appearance of *spurious* unphysical states, between the lowest bound state and the negative energy continuum [7]. This difficulty may arise from matrix representation solutions of the Dirac equation based on the minimization principle and only work rigorously if the spectrum has a lower bound. The Dirac spectrum is the complete set of positive and negative energy states together with the discrete spectrum of bound states. The whole spectrum is, therefore, needed due to the contribution of negative energy continuum states that can significantly improve the accuracy [8]. This problem has been studied by many authors since it was first observed. A common feature of all is ensuring that the nonrelativistic limit is correct. This requires a choice of basis function satisfying the kinetic-balance condition [9,10],

$$\lim_{c\to\infty} c\psi^S = \frac{1}{2m_0}\vec{\sigma}\cdot\hat{\vec{p}} \lim_{c\to\infty}\psi^L. \tag{5}$$

Note that the discussions on variational instability of the matrix representation for the Dirac equation are treated rigorously in the context of both chemistry [7,8,11–14] and mathematical physics [15,16] in recent publications.

Molecular wave functions to be used in the algebraic solution are obtained from a linear combination of atomic orbitals (LCAOs) [17,18], which are generally represented by analytical Gaussian-type [19] and exponential-type basis functions [20]. In relativistic structure calculations, the better

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choice is associated with the definition of the atomic nucleus model [21,22]. Brief information on that issue is given below. First it should be emphasized that the pointlike model of the nucleus is valid only for atoms with atomic number $Z, Z \leqslant Z_c$, where Z_c is the critical value of atomic number Z, $Z_c = \alpha^{-1} \simeq 137.04$, and α is the fine-structure constant. If $Z > \alpha^{-1}$, the results obtained are imaginary and they require quantum electrodynamics (QED) for interpretation [23]. The finite-size nucleus model may give more accurate values for large atomic numbers since it is a more realistic representation of the problem [22]; if the Dirac Hamiltonian is correctly defined as a self-adjoint operator, however, such difficulties are avoided [24–27]. The assertion that the Dirac equation of an electron moving through the Coulomb potential around a fixed-point-like nucleus is inconsistent has now been refuted [26].

Gaussian-type basis functions are a natural choice of basis function in a finite-size nucleus model [22]. Such a model removes the singularity of a basis function at the origin [22,28–30], which means the cusp [31] is no longer infinite. That leads to a faster convergence with fewer Gaussian-type basis functions. They also satisfy the condition of kinetic balance. This is due to the fact that the exponent n of power function r^n of the radial part of the unnormalized Gaussian-type basis function has the form

$$g_n(\zeta,r) = r^n e^{-\zeta r^2}, \tag{6}$$

which does not depend on the speed of light c [30]. Here, ζ is the orbital parameter.

Exponential-type functions, on the other hand, are linear combinations of hydrogen atom Hamiltonian eigenfunctions. The analytical properties of the resulting wave functions thus obey both the cusp condition at the nucleus [31] and exponential decay at long range [32]. They have a physically meaningful functional form, unlike Gaussian-type functions in a fixed-point-like nucleus model. This maintains the suitability of exponential-type orbitals in the theoretical approach to the Dirac equation, as described in the sections of Grant's textbook defining spinors ([11], Chap. 7). Applications to new advances in atomic, molecular, and nuclear physics such as laser-matter interaction have been studied [33], and electrons have been subjected to a very intense magnetic field [34]. Consider also exotic atoms which are very sensitive to quantum electrodynamic effects [35], e.g., the hydrogenlike muonium atom ($\mu^+ e^-$), which is the bound state of positive muon (μ^+) and an electron (e^-). It is an ideal test object for quantum electrodynamic studies since it is comprised of two pointlike particles without finite-size or internal structure [36].

The present study is first focused on the difficulties arising from variational solution of the Dirac equation using the fixed-point-like model of the nucleus. They were solved for hydrogenlike atoms by defining the Dirac-Coulomb differential equation and its solution, L spinors [11,37–39],

$$\frac{\partial}{\partial r} f^{\beta}_{n_r\kappa}(\zeta,r) = -\beta \frac{\kappa}{r} f^{\beta}_{n_r\kappa}(\zeta,r) + \left(\frac{\beta N_{n_r\kappa} - \gamma - n_r}{r} + \zeta \right) f^{-\beta}_{n_r\kappa}(\zeta,r), \tag{7}$$

$$f^{\beta}_{n_r\kappa}(\zeta,r) = \left[\frac{n_r!(2\gamma + n_r)}{2N_{n_r\kappa}(N_{n_r\kappa} - \kappa)\Gamma(2\gamma + n_r)} \right] (2\zeta r)^{\gamma} e^{-\zeta r} \times \left\{ -(1 - \delta_{n_r0}) L^{2\gamma}_{n_r-1}(2\zeta r) + \beta \left(\frac{N_{n_r\kappa} - \kappa}{n_r + 2\gamma} \right) L^{2\gamma}_{n_r}(2\zeta r) \right\}. \tag{8}$$

Here, n_r is the radial quantum numbers [40], with $n_r = n - |\kappa|$, and n the principal quantum number,

$$\gamma = \sqrt{\kappa^2 - \frac{Z^2}{c^2}}, \tag{9}$$

Z is the atomic number,

$$N_{n_r\kappa} = \sqrt{n_r^2 + 2n_r\gamma + \kappa^2}, \tag{10}$$

$\kappa = \{\pm 1, \pm 2, \ldots\}, \zeta$ is the orbital parameter, and $\beta = \pm 1$ represent large and small components of L spinors, respectively. Furthermore, $L^{\alpha}_{n}(x)$ are generalized Laguerre polynomials [41].

Here, it is observed that basis functions satisfying the Dirac-Coulomb equation can be generated which also solve the matrix form of the Dirac equation. These basis functions are obtained analogously to L spinors. They are referred to as Slater-type spinor orbitals and differ from S spinors [11] in that they satisfy the differential equation given for L spinors. This is achieved by generalizing the S spinor form to flexible exponent values.

In general, a power function such as $z^a = e^{a \log z}$ is analytic at $z_0 = 0$ if $a \in \mathbb{Z}$ is an integer [42]. This means that it can be represented near the origin by a convergent power series [43],

$$f_p(z) = \sum_{i=0}^{\infty} w_i (z - z_0)^i, \tag{11}$$

where z_0 is a constant, z varies around z_0, and w_i represents the coefficient of the ith term; they essentially correspond to the derivatives of f_p at z_0. It becomes apparent as a consequence of Eq. (11) that the exponential-type functions with integer principal quantum numbers possess an addition theorem, i.e., relations for products of two functions centered on different positions. The power of r, r^{γ}, occurring in Eq. (8), where γ in the set of real numbers ($\gamma \in \mathbb{R}$), is, on the other hand, nonanalytical. Thus, no meaningful power series for $f_p(r) = r^{\gamma}$ about $r = 0$ can exist [44,45]. So far, the problem of the evaluation of relativistic molecular integrals over exponential-type orbitals has been thought to be nearly insurmountable. Obtaining compact-form expressions for two-center one-electron relativistic molecular integrals is, therefore, the second topic of the present study.

II. SLATER-TYPE SPINOR ORBITALS IN THE TWO-COMPONENT FORMALISM

The Slater-type spinor orbitals (STSOs) which can be considered as relativistic analogues of Slater-type functions (STFs) have the functional form of nodeless L spinors, or those with the fewest nodes, characterized by minimum values of radial quantum numbers.

The STSOs used in this paper are defined as

$$\chi^{\beta}_{n\kappa m}(\zeta,\vec{r}) = f^{\beta}_{n\kappa}(\zeta,r)\Omega^{\beta}_{\kappa m}(\theta,\vartheta), \tag{12}$$

$$f^{\beta}_{n\kappa}(\zeta,r) = \{A^{\beta}_{n\kappa}r^{n} + \zeta B^{\beta}_{n\kappa}r^{n+1}\}e^{-\zeta r}, \tag{13}$$

where $\beta = \pm 1$ represent large and small components of STSOs, $n \in \mathbb{R}^{+}, \kappa = \{\pm 1, \pm 2, \ldots\}$, and $-|\kappa| + \frac{1}{2} \leqslant m \leqslant |\kappa| - \frac{1}{2}$ are the secondary total angular momentum quantum numbers, respectively.

The $\Omega^{\beta}_{\kappa m}$ are the spin-$\frac{1}{2}$ spinor spherical harmonics,

$$\Omega^{\beta}_{\kappa m}(\theta,\vartheta) = \sum_{\sigma=\mp\frac{1}{2}} C^{l_{\beta}\frac{1}{2}j}_{m-\sigma\sigma m} Y_{l_{\beta}m-\sigma}(\theta,\vartheta)\phi_{\sigma}, \tag{14}$$

$$\phi_{\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix}, \quad \phi_{-\frac{1}{2}} = \begin{pmatrix}0\\1\end{pmatrix}. \tag{15}$$

Here, the quantities C are Clebsch-Gordan coefficients. The spinor spherical harmonics can be obtained by the following formula using the explicit form of the Clebsch-Gordan coefficients [40,46]:

$$\begin{aligned}\Omega^{\beta}_{\kappa m}(\theta,\vartheta) &= \begin{bmatrix} a^{\beta}_{\kappa m}\eta_{m-\frac{1}{2}}Y_{l_{\beta}m-\frac{1}{2}}(\theta,\vartheta)\\ b^{\beta}_{\kappa m}\eta_{m+\frac{1}{2}}Y_{l_{\beta}m+\frac{1}{2}}(\theta,\vartheta)\end{bmatrix}\\ &= \begin{bmatrix} \mathrm{sgn}(-\beta|\kappa|)\eta_{\mathrm{m}-\frac{1}{2}}\sqrt{\frac{\beta|\kappa|+1/2-\mathrm{m}}{2\beta|\kappa|+1}}\mathrm{Y}_{\mathrm{l}_{\beta}\mathrm{m}-\frac{1}{2}}(\theta,\vartheta)\\ \eta_{m+\frac{1}{2}}\sqrt{\frac{\beta|\kappa|+1/2+m}{2\beta|\kappa|+1}}Y_{l_{\beta}m+\frac{1}{2}}(\theta,\vartheta)\end{bmatrix},\end{aligned} \tag{16}$$

where Y_{lm_l} are the complex spherical harmonics with orbital angular momentum l and magnetic quantum number m_l, with

$$l_{\beta} = \begin{cases} \beta|\kappa|, & \beta|\kappa| > 0\\ -\beta|\kappa| - 1, & \beta|\kappa| < 0, \end{cases} \tag{17}$$

and $\eta_m = (-1)^{(|m_l|-m_l)/2}$. Note that the definition of phases in this work for the complex spherical harmonics ($Y^{*}_{lm_l} = Y_{l-m_l}$) differs from the Condon-Shortley phases by sign factor $(-1)^{m_l}$ [47,48].

The spinor spherical harmonics satisfy the orthogonality relations,

$$\begin{aligned}\int_0^{\pi}\int_0^{2\pi} \Omega^{\beta\dagger}_{\kappa m}(\theta,\vartheta)\Omega^{\beta'}_{\kappa' m'}(\theta,\vartheta)d\Omega &= \delta_{\beta\kappa,\beta'\kappa'}\delta_{mm'},\\ d\Omega &= \sin\theta d\theta d\vartheta,\end{aligned} \tag{18}$$

and the angular part

$$\hat{T}_{\theta\vartheta} \equiv (\vec{\sigma}\cdot\hat{r}) = \begin{bmatrix}\cos\theta & \sin\theta e^{-i\vartheta}\\ \sin\theta e^{i\vartheta} & -\cos\theta\end{bmatrix} \tag{19}$$

of operator $(\vec{\sigma}\cdot\hat{\vec{p}}) \equiv \hat{T}_{r\theta\vartheta}$,

$$\begin{aligned}(\vec{\sigma}\cdot\hat{\vec{p}}) \equiv \hat{T}_{r\theta\vartheta} &= \left(\frac{\partial}{\partial r} + \frac{\vec{\sigma}\cdot\vec{l}}{r}\right)(\vec{\sigma}\cdot\hat{r}) \equiv \hat{T}_r\hat{T}_{\theta\vartheta}\\ &= \left(\frac{\partial}{\partial r} + \beta\frac{\kappa}{r}\right)\begin{bmatrix}\cos\theta & \sin\theta e^{-i\vartheta}\\ \sin\theta e^{i\vartheta} & -\cos\theta\end{bmatrix},\end{aligned} \tag{20}$$

changes their parity (odd),

$$\hat{T}_{\theta\vartheta}\Omega^{\beta}_{\kappa m}(\theta,\vartheta) = -\Omega^{-\beta}_{\kappa m}(\theta,\vartheta). \tag{21}$$

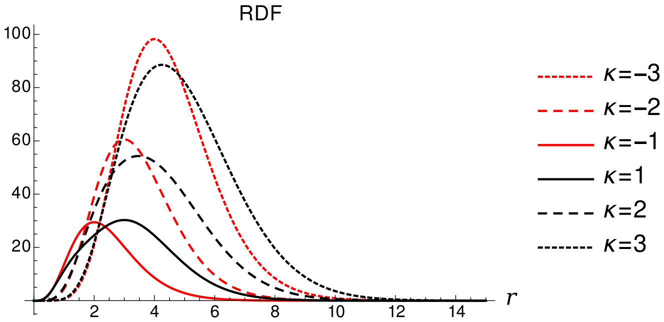

FIG. 1. Radial distribution functions [RDFs, $4\pi r^2 X^{\dagger}X, X^{\dagger} = (\chi^{1}\ \chi^{-1})$] for Slater-type relativistic spinor orbitals in atomic units (a.u.) where $n = \gamma$ and $Z = 1$.

The coefficients $A^{\beta}_{n\kappa}, B^{\beta}_{n\kappa}$ included in the radial part of the STSOs are defined as follows:

$$A^{\beta}_{n\kappa} = \begin{cases}\left(\frac{\beta\kappa}{2n}\right), & \kappa < 0\\ \frac{\beta}{2}(N_{n\kappa} - \kappa) - \frac{1}{2}, & \kappa > 0,\end{cases} \tag{22}$$

$$B^{\beta}_{n\kappa} = \begin{cases}0, & \kappa < 0\\ -\beta\left(\frac{N_{n\kappa}-\kappa}{2n+1}\right), & \kappa > 0,\end{cases} \tag{23}$$

and

$$N_{n\kappa} = \begin{cases}|\kappa|, & \kappa < 0\\ \sqrt{\kappa^2 + (2n+1)}, & \kappa > 0.\end{cases} \tag{24}$$

It should be emphasized that the STSOs have the same form as S spinors [11] when $n = \gamma = \sqrt{\kappa^2 - Z^2/c^2}$, except that their radial parts are coupled for large and small components under operation $\hat{T}_r$. They satisfy the system of differential equations given in Eq. (7) by the following formula (see also Fig. 1):

$$\begin{aligned}\frac{\partial}{\partial r}f^{\beta}_{n\kappa}(\zeta,r) = &-\beta\frac{\kappa}{r}f^{\beta}_{n\kappa}(\zeta,r)\\ &+\left(\frac{\beta N_{n\kappa} - n - \delta_{|\kappa|\kappa}}{r} + \zeta\right)f^{-\beta}_{n\kappa}(\zeta,r).\end{aligned} \tag{25}$$

III. SLATER-TYPE SPINOR ORBITALS IN THE FOUR-COMPONENT FORMALISM

The most rigorous way to calculate the relativistic molecular structure is to use the four-component formalism. It affords a physical clarity that is absent from the two-component reductions of the Dirac operator, especially with regard to the problems involved in the change of representation and the gauge dependence of the electromagnetic interaction [49,50]. Gaussian-type basis functions are used in a number of Dirac-Hartree-Fock programs [18,51–53], including both BERTHA [54,55] and DIRAC [56,57], to calculate the relativistic molecular structure through a four-component form of the Dirac equation.

The exponential-type orbitals, however, could not be used so far in the absence of basis functions permitting flexibility by providing coupling between large and small components.

Here, an adequate computational procedure to evaluate the molecular integrals is presented. The Slater-type spinor orbitals and the given relationship between their large and small components in Eq. (25) pave the way for such developments.

Expansion of the Dirac equation given in Eqs. (1) and (2) into the set of four coupled differential equations through the notation for first-order Cartesian derivatives,

$$\hat{T}^0 = \frac{\partial}{\partial z}, \quad \hat{T}^1 = \frac{\partial}{\partial x} + i\frac{\partial}{\partial y}, \quad \hat{T}^{-1} = \frac{\partial}{\partial x} - i\frac{\partial}{\partial y}, \tag{26}$$

is given as

$$\begin{aligned}(c\hbar/i)\{-\hat{T}^0\chi_2 + \hat{T}^1\chi_1\} &= \{E + m_0c^2 - V(\vec{r})\}\chi_4,\\ (c\hbar/i)\{\hat{T}^0\chi_1 + \hat{T}^{-1}\chi_2\} &= \{E + m_0c^2 - V(\vec{r})\}\chi_3,\\ (c\hbar/i)\{-\hat{T}^0\chi_4 + \hat{T}^1\chi_3\} &= \{E - m_0c^2 - V(\vec{r})\}\chi_2,\\ (c\hbar/i)\{\hat{T}^0\chi_3 + \hat{T}^1\chi_4\} &= \{E - m_0c^2 - V(\vec{r})\}\chi_1.\end{aligned} \tag{27}$$

Here, the four-component spinor wave function is thus represented by Slater-type spinor orbitals as follows:

$$X_{njlm}(\zeta,\vec{r}) = \begin{bmatrix}\chi_1\\ \chi_2\\ \chi_3\\ \chi_4\end{bmatrix} = \begin{bmatrix}\chi^{-10}_{nljm}(\zeta,\vec{r})\\ \chi^{-11}_{nljm}(\zeta,\vec{r})\\ \chi^{10}_{nljm}(\zeta,\vec{r})\\ \chi^{11}_{nljm}(\zeta,\vec{r})\end{bmatrix}$$

$$= \begin{bmatrix}f^{-1}_{nj}(\zeta,r)\Omega^{-10}_{ljm}(\theta,\vartheta)\\ f^{-1}_{nj}(\zeta,r)\Omega^{-11}_{ljm}(\theta,\vartheta)\\ f^{1}_{nj}(\zeta,r)\Omega^{10}_{ljm}(\theta,\vartheta)\\ f^{1}_{nj}(\zeta,r)\Omega^{11}_{ljm}(\theta,\vartheta)\end{bmatrix}, \tag{28}$$

where the quantum number j, which is yet to be defined, is the total angular momentum quantum number with $j = l \mp 1/2$ and $\beta = \pm 1$.

The radial and angular parts of Slater-type spinor orbitals in four-component formalism are

$$\chi^{\beta\lambda}_{n\kappa m}(\zeta,\vec{r}) = f^{\beta}_{nj}(\zeta,r)\Omega^{\beta\lambda}_{ljm}(\theta,\vartheta), \tag{29}$$

and in explicit form are given by

$$f^{\beta}_{nj}(\zeta,r) = \left\{A^{\beta}_{nj}r^{n} + \zeta B^{\beta}_{nj}r^{n+1}\right\}e^{-\zeta r}, \tag{30}$$

$$\Omega^{\beta\lambda}_{ljm}(\theta,\vartheta) = C^{\beta\lambda}_{ljm}Y_{l_\beta m(\lambda)}(\theta,\vartheta), \tag{31}$$

with $m_l = m(\lambda) = m + \lambda - 1/2$ and

$$C^{\beta\lambda}_{ljm} = (-1)^{1-\lambda}\eta_m\sqrt{\frac{l + (-1)^{\lambda}\beta m + \beta}{2l+1}}, \tag{32}$$

respectively.

Considering the system of differential equations given in Eq. (25) and the expressions for Cartesian derivatives of wave functions in spherical polar coordinates [58], the following relations are obtained for the left-hand side of Eq. (27):

$$\begin{aligned}\hat{T}^{\alpha\alpha'}\chi_{pp'} &= \frac{c\hbar}{i}\{\epsilon_p\hat{T}^{\alpha}\chi_p + \hat{T}^{\alpha'}\chi_{p'}\}\\ &= \frac{c\hbar}{i}\left\{\epsilon_p D^{\alpha}_{pq} + D^{\alpha'}_{p'q}\right\}\chi_q,\end{aligned} \tag{33}$$

where $\epsilon_p = \mp, \{\alpha,\alpha'\} = 0, \mp 1$, the indices $\{p,p';q,q'\}$ are used to represent the components of the four-component Slater-type spinor orbitals, and $D^{\alpha}_{pq}, D^{\alpha'}_{p'q'}$ are referred to as coupling functions, respectively.

Equation (33) is the compact form of the left-hand side of the four coupled differential equations given in Eq. (27). Accordingly, Eq. (27) is rewritten as follows (see Appendix A):

$$\frac{c\hbar}{i}\left\{\epsilon_p D^{\alpha}_{pq} + D^{\alpha'}_{p'q}\right\}\chi_q = \{E + \epsilon_q m_0c^2 - V(\vec{r})\}\chi_q. \tag{34}$$

IV. ALGEBRAIC SOLUTION OF THE DIRAC EQUATION

The basis-set expansion method is commonly preferred either in nonrelativistic or relativistic molecular structure calculations.

The two-component form of four-component molecular spinors with index p is

$$X_p = \begin{pmatrix}X^{-1}_p\\ X^{+1}_p\end{pmatrix} \tag{35}$$

and are, therefore, expanded in term of Slater-type spinors as follows:

$$X^{-1}_p = \sum_q^N \chi^{-1}_q C^{-1}_{pq}, \tag{36}$$

$$X^{+1}_p = \sum_q^N \chi^{+1}_q C^{+1}_{pq}, \tag{37}$$

where $C^{\pm 1}_{pq}$ are the linear combination coefficients. They are used throughout the calculation of electronic energies of one-electron atoms and homonuclear and heteronuclear diatomic molecules as

$$\begin{aligned}X^{\beta}_{p,\mathcal{I}} = i^{(1-\delta_{|\beta|\beta})}\Bigg[&\sum_q^N \frac{1}{r_a}\chi^{\beta}_q(\zeta_a,\vec{r}_a)C^{\beta}_{pq,\mathcal{I}}\\ &+ \mathcal{I}\sum_q^N \frac{1}{r_b}\chi^{\beta}_q(\zeta_b,\vec{r}_b)C^{\beta}_{pq,\mathcal{I}}\Bigg],\end{aligned} \tag{38}$$

$$X^{\beta}_p = i^{(1-\delta_{|\beta|\beta})}\left[\sum_{qk}^N \frac{1}{r_k}\chi^{\beta}_q(\zeta_q,\vec{r}_k)C^{\beta,k}_{pq}\right]. \tag{39}$$

Or, more explicitly,

$$X_p = \left\{\begin{array}{lccccccccccc} q: & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & \ldots & N\\ \chi_q: & \chi_1 & \chi_2 & \chi_3 & \chi_4 & \chi_5 & \chi_6 & \chi_7 & \chi_8 & \chi_9 & \ldots & \chi_N\\ n\kappa: & 1-1 & 2-1 & 11 & 2-2 & 3-1 & 21 & 3-2 & 22 & 3-3 & \ldots & N-N\end{array}\right\}, \tag{40}$$

where $k = a,b$; the vectors $\vec{r}_a$ and $\vec{r}_b$ are distances of the electron from the nuclei a; $b,\mathcal{I} = \mp 1$ denote the gerade, ungerade states; and N is the upper limit of the summation, respectively.

The Rayleigh quotient of the Dirac operator with STSOs in matrix form is

$$R(\chi) = \frac{\langle \chi \mid \hat{H}_D \mid \chi \rangle}{\langle \chi \mid \chi \rangle} = \frac{C^{\dagger} \hat{H}_D C}{C^{\dagger} C}. \tag{41}$$

Regarding Eq. (41), the generalized eigenvalue equation in compact and its matrix form can be written as [17,18]

$$(H'_D - \epsilon S)C = 0, \tag{42}$$

or, more explicitly, with indexes p and q,

$$\sum_{q}^{N} (H'_{D\,pq} - \epsilon_p S_{pq} C_{pq}) = 0. \tag{43}$$

Here, C_{pq} can be expressed in terms of the coefficients defined in Eqs. (36) and (37),

$$C_{pq} = \begin{pmatrix} C^{\beta}_{pq} \\ C^{-\beta}_{pq} \end{pmatrix} \tag{44}$$

and

$$H'_{D\,pq} = \begin{pmatrix} V^{\beta\beta}_{pq} & cT^{\beta-\beta}_{pq} \\ cT^{-\beta\beta}_{pq} & -2m_0c^2 S^{-\beta-\beta}_{pq} + V^{-\beta-\beta}_{pq} \end{pmatrix}, \tag{45}$$

$$S_{pq} = \begin{pmatrix} S^{\beta\beta}_{pq} & 0 \\ 0 & S^{-\beta-\beta}_{pq} \end{pmatrix}. \tag{46}$$

$H'_{D\,pq}$ and $S^{\beta\beta'}_{pq}$, $\beta' = \pm\beta$, $\beta = \pm 1$, are the real symmetric matrices whose nonzero $N \times N$ submatrices in atomic units (a.u.) have the following elements.

For one-electron atoms,

$$S^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta,\zeta') = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r})\chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r})dV, \tag{47}$$

$$V^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta,\zeta') = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r})\left(-\frac{Z}{r}\right)\chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r})dV, \tag{48}$$

$$T^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta,\zeta') = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r})(\vec{\sigma}\cdot\hat{\vec{p}})\chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r})dV, \tag{49}$$

and for one-electron diatomic molecules,

$$S^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_a,\zeta_b,\vec{R}_{ab}) = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r}_a)\chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r}_b)dV, \tag{50}$$

$$\begin{aligned}{}^{abb}V^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_a,\zeta_b,\vec{R}_{ab}) = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r}_a)\left(-\frac{Z_b}{r_b}\right) \\ \times\ \chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r}_b)dV,\end{aligned} \tag{51}$$

$$\begin{aligned}{}^{aab}V^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_a,\zeta'_a,\vec{R}_{ab}) = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r}_a)\left(-\frac{Z_b}{r_b}\right) \\ \times\ \chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r}_a)dV,\end{aligned} \tag{52}$$

$$\begin{aligned}T^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_a,\zeta_b,\vec{R}_{ab}) = \int \chi^{\beta\dagger}_{n\kappa m}(\zeta,\vec{r}_a)(\vec{\sigma}\cdot\hat{\vec{p}}) \\ \times\ \chi^{\beta'}_{n'\kappa'm'}(\zeta',\vec{r}_b)dV.\end{aligned} \tag{53}$$

S,V,T are the integrals referred to as overlap, nuclear attraction, and kinetic energy integrals, with $\vec{R}_{ab} = \vec{r}_a - \vec{r}_b$ the internuclear distance vector, respectively.

V. EVALUATION OF ONE-ELECTRON MOLECULAR INTEGRALS

The relativistic molecular integrals defined in Eqs. (50)–(53) are reduced to the linear combinations of nonrelativistic molecular integrals over Slater-type functions with noninteger values of the leading exponents by considering the definitions given in Eqs. (12)–(25) as follows. The overlap integrals are

$$\begin{aligned}&S^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ &\quad= \mathcal{N}^{\beta}_{n\kappa}(\zeta_A)\mathcal{N}^{\beta'}_{n'\kappa'}(\zeta_B)\big(a^{\beta}_{\kappa m}a^{\beta'}_{\kappa'm'} + b^{\beta}_{\kappa m}b^{\beta'}_{\kappa'm'}\big) \\ &\quad\times\ (X^{\dagger}S_{-} + X^{\dagger}S_{+}),\end{aligned} \tag{54}$$

$$S = \begin{bmatrix} S_{nlm_l,n'l'm_{l'}}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ S_{n+1lm_l,n'l'm_{l'}}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ S_{nlm_l,n'+1l'm_{l'}}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ S_{n+1lm_l,n'+1l'm_{l'}}(\zeta_A,\zeta_B,\vec{R}_{AB}) \end{bmatrix}. \tag{55}$$

The nuclear attraction integrals defined in Eqs. (51) and (52) can be expressed in terms of overlap integrals and by the following formulas:

$$\begin{aligned}&{}^{aab}V^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_A,\zeta'_A,\vec{R}_{AB}) \\ &\quad= \mathcal{N}^{\beta}_{n\kappa}(\zeta_A)\mathcal{N}^{\beta'}_{n'\kappa'}(\zeta'_A)\big(a^{\beta}_{\kappa m}a^{\beta'}_{\kappa'm'} + b^{\beta}_{\kappa m}b^{\beta'}_{\kappa'm'}\big) \\ &\quad\times\ (X^{\dagger}\ V_{-} + X^{\dagger}\ V_{+}),\end{aligned} \tag{56}$$

$$V = \begin{bmatrix} V_{nlm_l,n'l'm_{l'}}(\zeta_A,\zeta'_A,\vec{R}_{AB}) \\ V_{n+1lm_l,n'l'm_{l'}}(\zeta_A,\zeta'_A,\vec{R}_{AB}) \\ V_{nlm_l,n'+1l'm_{l'}}(\zeta_A,\zeta'_A,\vec{R}_{AB}) \\ V_{n+1lm_l,n'+1l'm_{l'}}(\zeta_A,\zeta'_A,\vec{R}_{AB}) \end{bmatrix}. \tag{57}$$

The expression for kinetic energy integrals can then easily be obtained through Eq. (25) as

$$\begin{aligned}&T^{\beta\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ &\quad= -\{N_{n'\kappa'} - \beta'(n' + \delta_{|\kappa'|\kappa'})\}{}^{abb}V^{\beta-\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_A,\zeta_B,\vec{R}_{AB}) \\ &- (\zeta_B)S^{\beta-\beta'}_{n\kappa m,n'\kappa'm'}(\zeta_A,\zeta_B,\vec{R}_{AB}),\end{aligned} \tag{58}$$

where $\mathcal{N}^{\beta}_{n\kappa}(\zeta)$ are normalization constants,

$$\mathcal{N}^{\beta}_{n\kappa}(\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{\mathrm{N}^{\beta}_{n\kappa}}}, \tag{59}$$

$$\begin{aligned}N^{\beta}_{n\kappa} &= \big(A^{\beta}_{n\kappa}\big)^2\Gamma[2n+1] + A^{\beta}_{n\kappa}B^{\beta}_{n\kappa}\Gamma[2n+2] \\ &+ \big(B^{\beta}_{n\kappa}\big)^2\frac{\Gamma[2n+3]}{4}.\end{aligned} \tag{60}$$

X,S_-,S_+,V_-,V_+ are the matrices corresponding to the coefficients of Slater-type spinor orbitals $A^{\beta}_{n\kappa}$ and $B^{\beta}_{n\kappa}$,

$$X = \begin{bmatrix} A^{\beta}_{n\kappa} A^{\beta'}_{n'\kappa'} \\ \zeta_B B^{\beta}_{n\kappa} A^{\beta'}_{n'\kappa'} \\ \zeta_B A^{\beta}_{n\kappa} B^{\beta'}_{n'\kappa'} \\ \zeta_B^2 B^{\beta}_{n\kappa} B^{\beta'}_{n'\kappa'} \end{bmatrix}, \qquad (61)$$

the nonrelativistic two-center overlap, and nuclear attraction integrals, respectively (see Appendix C for their explicit forms).

VI. RESULTS AND DISCUSSIONS

In this section, a number of one-electron systems are benchmarked to confirm the accuracy of the approach presented here. Whenever possible, its originality and its potential generalization are stressed.

Numerical approaches (e.g., finite-difference and finite-element methods) were used to obtain an accurate solution for the Dirac equation since it has an intricate matrix structure [59–67]. They are commonly carried out for ground states of one-electron systems, especially hydrogenlike atoms and one-electron diatomic molecules. A comprehensive calculation using this approach can be found in [67] (and references therein) using a B-spline basis function expansion, and here, in particular, the excited states also have been presented accurately. Large storage requirements as well as removing the singularities in the nuclear potentials restrict accurate solutions obtained using the numerical treatment to very small systems [61], i.e., an atom or a molecule with, at most, a few electrons distributed around two or three nuclei. These restrictions emphasize the vital importance of the algebraic approach. So far, an algebraic solution of the Dirac equation has not been generally applied successfully due to problems related to variational collapse. In the molecular context, these studies are difficult when the multicenter integrals are required in exponential-type basis functions. Rather than improving well-known approximations, the present study is therefore developed as an alternative to the algebraic approximation. It is focused on overcoming the difficulties discussed above.

Recently, an accurate evaluation of molecular integrals was provided in [68–70]. We believe this is the ideal starting point to reconsider application of kinetically balanced exponential-type spinor orbitals in the algebraic solution of the Dirac equation. Although the S spinors appear well suited to this problem, the difficulties of finding relations for two-center relativistic integrals remain if the large and small components of spinor orbitals used are independent. The S spinors are also restricted concerning orbital parameter optimization since the principal quantum numbers n of radial functions are determined by $n = \gamma$. The principal quantum numbers in Slater-type spinor orbitals, on the other hand, may have values independent of the speed of light and they satisfy the system of differential equations given for L spinors. They therefore *naturally* also satisfy the kinetic-balance condition. The Slater-type spinor orbitals and given relation in Eq. (25) for their large and small components also provide an efficient and simple method to evaluate relativistic molecular integrals.

TABLE I. State classifications for relativistic one-electron atoms and linear diatomic molecules.

κ	lj[a]	$l\Lambda$[b]
-1	s	$s\sigma$
1	$\tilde{p}$	$\tilde{p}\sigma$
-2	p	$p\pi$
2	$\tilde{d}$	$\tilde{d}\pi$
-3	d	$d\delta$
3	$\tilde{f}$	$\tilde{f}\delta$
-4	f	$f\phi$
4	$\tilde{g}$	$\tilde{g}\phi$
-5	g	$g\gamma$

[a] $j = |\kappa| - \frac{1}{2}$; $l = j - \frac{|\beta|}{2}$; $\tilde{l} = j + \frac{|\beta|}{2}$

[b]

Λ	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
State	σ	π	δ	ϕ	γ

In this study, Eq. (42) is comprised of matrix elements which are solved to determine linear combination coefficients and electronic energies using the MATHEMATICA programming language [71]. Schur decomposition [72] enabled us to obtain eigenvalues. The calculations are performed for ground and excited states of one-electron atoms and diatomic molecules with the single-ζ basis-set approximation in linear combinations of Slater-type spinor orbitals given in Eqs. (38) and (39) for each sign of κ. The determination of nonlinear parameters is of critical importance for correct representation of atomic orbitals in relativistic calculations. The orbital parameters are allowed to be variational optimum values. The Powell optimization procedure [73] is used for the defined basis-set approximation. The quantum numbers n are also chosen to take positive integer values to show the basis functions to be used in the solution of the Dirac equation satisfying the kinetic-balance condition. Note that n can be assigned as $n = \gamma = \sqrt{\kappa^2 - Z^2/c^2}$ or set as a parameter to be optimized. All results are given in atomic units (a.u.) using $c = 137.035\,999\,139$ (speed of light), from a recent value for the inverse fine-structure constant [74].

In Table I, the state classifications of relativistic one-electron atoms and linear diatomic molecules are presented in both two- and four-component formalisms. The orbital configurations, denoted by the tilde, are used to represent positive values of κ, where total angular momentum quantum numbers j have $j = l - 1/2$ values. In the last column of this table, the orbital configuration of linear diatomic molecules is represented by the united atom state and molecular symmetry notations.

The results obtained for one-electron atoms with the extended basis-set approximation are given in Eq. (38)–(40), where $a = b$ and κ take positive and negative values for ground and excited energy states. They are presented in Fig. 2 and Tables II–IV with 15-digit precision. The correct digits are underlined. Note that in all calculations, it is confirmed for the kinetic energy matrix that $T^{\beta-\beta}_{pq} = T^{-\beta\beta\dagger}_{pq}, \beta = \pm 1$, so the Hamiltonian matrix as a whole is a real symmetric matrix.

In Tables II and III, electronic ground-state energies (lowest positive energy spectrum eigenvalues), the highest negative

TABLE II. The results of computations for the lowest eigenvalue in the positive energy spectrum ($|\epsilon_q^{-1}|$) and highest eigenvalue of the negative energy spectrum ($|\epsilon_q^{+1}|$) of a hydrogen (H) atom in atomic units (a.u.).

N	ϵ_q^{-1}	ϵ_q^{+1}
	$\underline{0.5.00006\ 65659\ 65473}$	$\underline{37557.7\ 30120\ 04801}$
1	$\underline{0.500006\ 656}49\ 85350$	$\underline{37557.7\ 3012}1\ 04802$
	$\underline{0.500006\ 65659}\ 57503$	$\underline{37557.7\ 3012}1\ 04804$
4	$\underline{0.500006\ 656}47\ 83872$	$\underline{37557.7\ 30120}\ 47067$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 47067$
9	$\underline{0.500006\ 65659\ 6547}2$	$\underline{37557.7\ 30120}\ 30579$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 30579$
16	$\underline{0.500006\ 6565}6\ 24173$	$\underline{37557.7\ 30120}\ 23060$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 23060$
25	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 18827$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 18827$
36	$\underline{0.500006\ 6565}8\ 25382$	$\underline{37557.7\ 30120}\ 16136$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 16136$
49	$\underline{0.500006\ 65659\ 65473}$	$\underline{37557.7\ 30120}\ 14284$
	$\underline{0.500006\ 65659\ 65473}$	$\underline{3.75577\ 30120}\ 14284$

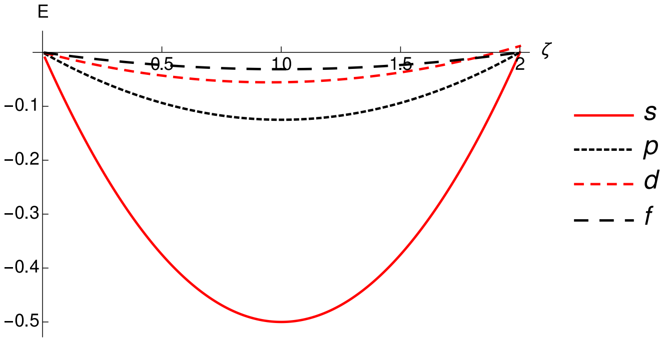

FIG. 2. The spectrum for a hydrogen atom (H) depending on orbital parameters in atomic units (a.u.) where the upper limit of summation N is 16 and the highest value of principal quantum number n is 4.

energy eigenvalue of the negative energy spectrum for one-electron atoms with atomic numbers $Z = 1$ (hydrogen atom) and $Z = 50$ (hydrogenlike tin atom) depending on the upper limit of summation N (values are given in the first column), and eigenvalues are listed in the second column. The first row of these tables indicates solutions obtained from the analytical formula for the atomic binding energy [11],

$$E_{nj} = -m_0c^2\left(1-\left\{1+\left[\frac{\frac{Z}{c}}{n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^2-\left(\frac{Z}{c}\right)^2}}\right]\right\}^{-1/2}\right), \tag{62}$$

and $-2m_0c^2$ [the values given in the table are in atomic units (a. u.), where $m_0 = 1$]. The principal quantum number n of the Slater-type orbitals is chosen to take $n = \gamma$ and integer values for each upper limit of summation given in the table. Variationally optimum values of orbital parameters are used throughout the ground energy state energy calculations and they are obtained via Powell's optimization method. It can be seen from these tables that the highest negative energy eigenvalue of the negative energy spectrum is always smaller than $(-2m_0c^2)$, which means that the positive energy spectrum has a lower bound greater than $(-m_0c^2)$. The electronic ground-state energy of atoms can therefore be calculated accurately using Slater-type spinor orbitals. The basis functions with integer values of quantum numbers satisfy the kinetic-balance condition and do not suffer from variational collapse. They may therefore also be convenient to investigate relativistic electronic structure calculations.

In Table IV, the results obtained for the first 14 excited electronic energy state eigenvalues of one-electron atoms are presented for atomic numbers $Z = 1$ and $Z = 50$. The first row of each given energy state is the results obtained from the analytical formula. The principal quantum number n for the Slater-type orbitals is chosen to take $n = \gamma$ values. The orbital parameters take values according to the formula $\zeta = Z/n$. The upper limit of summation N in linear combinations of atomic orbitals is determined as $N = 169$, which means the highest values of the principal quantum number are $n = 13$. Notice that the principal quantum number n used in the Slater-type orbitals [Eq. (12)] and n used in orbital configuration notation are not exactly the same. The n in orbital configuration notation takes values determined by Summerfeld's formula. It can be seen from this table that correct representation of electronic energy states of one-electron atoms using Slater-type spinor orbitals is possible via the algebraic approximation. The Dirac equation is compatible with the Rayleigh-Ritz method for an extended basis-set approximation, where κ can possess both positive and negative values.

In Fig. 2, some electronic energy excited states of the hydrogen atom ($Z = 1$) are plotted depending on orbital parameters in order to investigate the variational stability of calculations through solution of the generalized eigenvalue equation.

The calculations are also performed for one-electron diatomic molecules. This provides an extension to the approach described here to two-center systems. They are presented in Figs. 3 and 4, respectively.

In Fig. 3, the data for the ground and excited energy states of the one-electron hydrogen molecule ion (H_2^+) are given, depending on orbital parameters with various values of

TABLE III. The results of computations for the lowest eigenvalue in the positive energy spectrum ($|\epsilon_q^{-1}|$) and highest eigenvalue of the negative energy spectrum ($|\epsilon_q^{+1}|$) of tin (Sn^{49+}) atom in atomic units (a.u.).

N	ϵ_q^{-1}	ϵ_q^{+1}
	1294.62 61491 49721	37557.7 30120 04801
1	1294.62 61488 57124	37557.7 30170 04802
	1294.62 61491 20039	37557.7 30173 75028
4	1292.55 34167 07837	37557.7 30141 18050
	1294.62 61491 49720	37557.7 30141 73861
9	1294.62 61491 41207	37557.7 30132 93666
	1294.62 61491 49719	37557.7 30133 11397
16	1294.15 00111 11481	37557.7 30129 17719
	1294.62 61491 49721	37557.7 30129 25481
25	1294.62 61491 46951	37557.7 30127 06059
	1294.62 61491 49721	37557.7 30127 10127
36	1294.45 79183 57612	37557.7 30125 71504
	1294.62 61491 49721	3.75577 30125 73897
49	1294.62 61491 49721	37557.7 30124 78911
	1294.62 61491 49721	37557.7 30124 80438

internuclear distance. Figures are plotted with a resolution of 1/100. The variational stability of solutions for the generalized eigenvalue problem is examined in this figure. In Fig. 4, dependence on the internuclear distance of the electronic (E_e) and total ($E_T = E_e + 1/R$) ground-state energies of the one-electron hydrogen molecule ion are plotted.

In order to derive a coupled differential equation equivalent to Eq. (25), the two-center potential $V(r_A,r_B) = V(r_A) + V(r_B)$ needs to be expanded through multiple expansion [23,75,76]. The relations given and results presented in this paper demonstrate that accurate values for energies of diatomic molecules can be obtained. In the future, the performance of detailed calculations for diatomic molecules is planned.

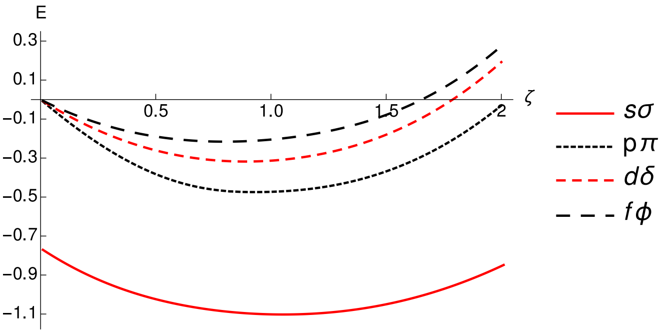

FIG. 3. The spectrum of the hydrogen molecule ion ($H_2{}^+$) depending on orbital parameters in atomic units (a.u.) where the upper limit of summation N is 16 and the highest value of principal quantum number n is 4.

TABLE IV. Results of computations for the electronic energy spectrum ($|\epsilon_q^{-1}|$) of H and Sn^{49+} atoms in atomic units (a.u.), respectively.

States (nl_j)	$Z = 1$	$Z = 50$
$1s_{1/2}$	00.500006 65659 65473	1294.62 61491 49721
	00.500006 65659 65473	1294.62 61491 49721
$2s_{1/2}$	00.125002 08018 91904	326.494 80404 98470
	00.125002 08018 91904	326.494 80456 50606
$2p_{1/2}$	00.125002 08018 91904	326.494 80404 98470
	00.125002 08018 91892	326.494 77551 54269
$2p_{3/2}$	00.125000 41602 89761	315.144 35481 19763
	00.125000 41602 89761	315.144 35481 19763
$3s_{1/2}$	0.0555562 95176 42162	143.829 80095 05448
	0.0555566 44825 53079	143.830 33870 33687
$3p_{1/2}$	0.0555562 95176 42162	143.829 80095 05448
	0.0555562 95176 41841	143.829 70779 53930
$3p_{3/2}$	0.0555558 02091 36667	140.457 87335 55951
	0.0555558 02091 36667	140.457 87335 87266
$3d_{3/2}$	0.0555558 02091 36667	140.457 87335 55951
	0.0555558 02091 36667	140.457 87328 61010
$3d_{5/2}$	0.0555556 37733 81484	139.406 33566 64720
	0.0555556 37733 81484	139.406 33566 64720
$4s_{1/2}$	0.0312503 38029 12509	80.3703 31292 25385
	0.0312507 96787 87140	80.3714 93791 66328
$4p_{1/2}$	0.0312503 38029 12509	80.3703 31292 25385
	0.0312503 38029 11933	80.3701 74609 46500
$4p_{3/2}$	0.0312501 30009 09831	78.9520 57930 40804
	0.0312501 57156 41757	78.9521 23798 86756
$4d_{3/2}$	0.0312501 30009 09831	78.9520 57930 40804
	0.0312501 30009 09828	78.9520 57524 20862
$4d_{5/2}$	0.0312500 60670 67921	78.5071 98898 95797
	0.0312500 60670 67921	78.5071 98899 03508

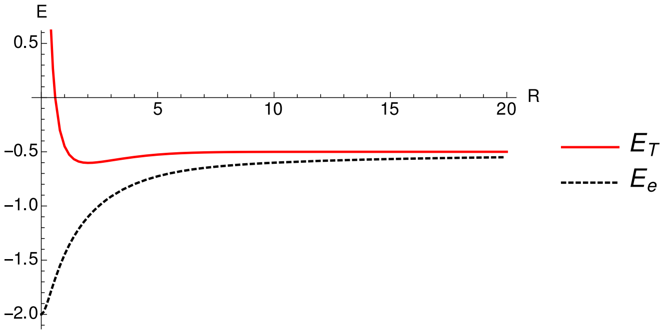

FIG. 4. Dependence of the ground-state total (E_T) and electronic (E_e) energies of the hydrogen molecule ion ($H_2{}^+$) on internuclear distance R for $0 \leqslant R \leqslant 20$ in atomic units (a.u.). The upper limit of the summation is $N = 16$ and the maximum principal quantum number is $n = 4$.

APPENDIX A: THE SLATER-TYPE SPINOR ORBITALS IN THE FOUR-COMPONENT FORMALISM

Taking into account the Cartesian derivatives of the wave function in terms of spherical polar coordinates [58],

$$\frac{\partial}{\partial x}=\sin\theta\cos\vartheta\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\cos\vartheta\frac{\partial}{\partial\theta}-\frac{1}{r}\frac{\sin\vartheta}{\sin\theta}\frac{\partial}{\partial\vartheta}, \tag{A1}$$

$$\frac{\partial}{\partial y}=\sin\theta\sin\vartheta\frac{\partial}{\partial r}+\frac{1}{r}\cos\theta\cos\vartheta\frac{\partial}{\partial\theta}-\frac{1}{r}\frac{\cos\vartheta}{\sin\theta}\frac{\partial}{\partial\vartheta}, \tag{A2}$$

$$\frac{\partial}{\partial z}=\cos\theta\frac{\partial}{\partial r}-\frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}, \tag{A3}$$

the relationships for the left-hand side of Eq. (27) are given as

$$\begin{aligned}\hat{T}^{0}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\} &= C_{ljm}^{\beta\lambda}\frac{\partial}{\partial_z}\big\{f_{nj}^{\beta}(\zeta,r)Y_{lm(\lambda)}(\theta,\vartheta)\big\}\\ &= C_{ljm}^{\beta\lambda}\Bigg\{\left(\frac{\beta N_{nj}-n-1}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}+m(\lambda)+1][l_{\beta}-m(\lambda)+1]}{(2l_{\beta}+3)(2l_{\beta}+1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+1\,m(\lambda)}(\theta,\vartheta)\\ &\quad+\left(\frac{\beta N_{nj}-n}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}+m(\lambda)][l_{\beta}-m(\lambda)]}{(2l_{\beta}+1)(2l_{\beta}-1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}-1\,m(\lambda)}(\theta,\vartheta)\Bigg\},\end{aligned} \tag{A4}$$

$$\begin{aligned}\hat{T}^{1}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\} &= C_{ljm}^{\beta\lambda}\frac{\partial}{\partial_z}\big\{f_{nj}^{\beta}(\zeta,r)Y_{lm(\lambda)}(\theta,\vartheta)\big\}\\ &= C_{ljm}^{\beta\lambda}\Bigg\{\left(\frac{\beta N_{nj}-n-1}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}+m(\lambda)+2][l_{\beta}+m(\lambda)+1]}{(2l_{\beta}+3)(2l_{\beta}+1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+1\,m(\lambda)+1}(\theta,\vartheta)\\ &\quad-\left(\frac{\beta N_{nj}-n}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}-m(\lambda)][l_{\beta}-m(\lambda)-1]}{(2l_{\beta}+1)(2l_{\beta}-1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}-1\,m(\lambda)+1}(\theta,\vartheta)\Bigg\},\end{aligned} \tag{A5}$$

$$\begin{aligned}\hat{T}^{-1}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\} &= C_{ljm}^{\beta\lambda}\frac{\partial}{\partial_z}\big\{f_{nj}^{\beta}(\zeta,r)Y_{lm(\lambda)}(\theta,\vartheta)\big\}\\ &= C_{ljm}^{\beta\lambda}\Bigg\{-\left(\frac{\beta N_{nj}-n-1}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}-m(\lambda)+2][l_{\beta}-m(\lambda)+1]}{(2l_{\beta}+3)(2l_{\beta}+1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+1\,m(\lambda)-1}(\theta,\vartheta)\\ &\quad+\left(\frac{\beta N_{nj}-n}{r}+\zeta\right)\sqrt{\frac{[l_{\beta}+m(\lambda)][l_{\beta}+m(\lambda)-1]}{(2l_{\beta}+1)(2l_{\beta}-1)}}f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}-1\,m(\lambda)-1}(\theta,\vartheta)\Bigg\}.\end{aligned} \tag{A6}$$

It is more advantageous to continue with the following compact form expressions of Eqs. (A4)–(A6):

$$\hat{T}^{0}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\}=C_{ljm}^{\beta\lambda}a_{njlm(\lambda)}^{\beta k}(\zeta,r)f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+k\,m(\lambda)}(\theta,\vartheta), \tag{A7}$$

$$\hat{T}^{1}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\}=C_{ljm}^{\beta\lambda}b_{njlm(\lambda)}^{\beta k}(\zeta,r)f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+k\,m(\lambda)+1}(\theta,\vartheta), \tag{A8}$$

$$\hat{T}^{-1}\big\{f_{nj}^{\beta}(\zeta,r)\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)\big\}=C_{ljm}^{\beta\lambda}c_{njlm(\lambda)}^{\beta k}(\zeta,r)f_{nj}^{-\beta}(\zeta,r)Y_{l_{\beta}+k\,m(\lambda)-1}(\theta,\vartheta), \tag{A9}$$

where $-1\leqslant k(2)\leqslant 1$. Note that the given number in parentheses for a sum indicates the step size. Writing the following relations as an example for the second and fourth terms of the left-hand side of Eq. (27), with $f_{nj}^{\beta}\equiv f_{nj}^{\beta}(\zeta,r)$, $\Omega_{ljm}^{\beta\lambda}\equiv\Omega_{ljm}^{\beta\lambda}(\theta,\vartheta)$, $Y_{lm(\lambda)}\equiv Y_{lm(\lambda)}(\theta,\vartheta)$, $a_{njlm(\lambda)}^{\beta k}\equiv a_{njlm(\lambda)}^{\beta k}(\zeta,r)$, $b_{njlm(\lambda)}^{\beta k}\equiv b_{njlm(\lambda)}^{\beta k}(\zeta,r)$, and $c_{njlm(\lambda)}^{\beta k}\equiv c_{njlm(\lambda)}^{\beta k}(\zeta,r)$, respectively,

$$\hat{T}^{0}\big(f_{nj}^{\beta}\Omega_{ljm}^{\beta\lambda}\big)+\hat{T}^{1}\big(f_{nj}^{\beta}\Omega_{ljm}^{\beta\lambda'}\big)=\big(C_{ljm}^{\beta\lambda}a_{njlm(\lambda)}^{\beta k}+C_{ljm}^{\beta\lambda'}b_{njlm(\lambda')}^{\beta k}\big)f_{nj}^{-\beta}Y_{l_{\beta}+k\,m(\lambda)}, \tag{A10}$$

$$\hat{T}^{0}\big(f_{nj}^{\beta}\Omega_{ljm}^{\beta\lambda}\big)+\hat{T}^{-1}\big(f_{nj}^{\beta}\Omega_{ljm}^{\beta\lambda'}\big)=\big(C_{ljm}^{\beta\lambda}a_{njlm(\lambda)}^{\beta k}+C_{ljm}^{\beta\lambda'}c_{njlm(\lambda')}^{\beta k}\big)f_{nj}^{-\beta}Y_{l_{\beta}+k\,m(\lambda)}, \tag{A11}$$

where the results should be multiplied by $(-1)^{[|m(\lambda)|-m(\lambda)]/2}$. Considering Eq. (27) and Eqs. (A4)–(A6), it is easy to see that $m(\lambda)=m(\lambda')\mp 1$.

APPENDIX B: THE QUESTION OF KINETIC BALANCE

The matrix representation of the Dirac equation for an electron moving through the Coulomb potential around a fixed nucleus in two-component form [12],

$$\begin{pmatrix} V_{pq}^{\beta\beta}+m_0c^2S_{pq}^{\beta\beta} & cT_{pq}^{\beta-\beta} \\ cT_{pq}^{-\beta\beta} & V_{pq}^{-\beta-\beta}-m_0c^2S_{pq}^{-\beta-\beta} \end{pmatrix}\begin{pmatrix} C_{pq}^{\beta} \\ C_{pq}^{-\beta} \end{pmatrix}=\begin{pmatrix} \epsilon_p^{\beta} \\ \epsilon_p^{-\beta} \end{pmatrix}\begin{pmatrix} S_{pq}^{\beta\beta} & 0 \\ 0 & S_{pq}^{-\beta-\beta} \end{pmatrix}\begin{pmatrix} C_{pq}^{\beta} \\ C_{pq}^{-\beta} \end{pmatrix}, \tag{B1}$$

may be written in the following forms:

$$\big(V_{pq}^{\beta\beta}+m_0c^2S_{pq}^{\beta\beta}\big)C_{pq}^{\beta}+cT_{pq}^{\beta-\beta}C_{pq}^{-\beta}=\epsilon_p^{\beta}S_{pq}^{\beta\beta}C_{pq}^{\beta}, \tag{B2a}$$

$$cT_{pq}^{-\beta\beta}C_{pq}^{\beta}+\big(V_{pq}^{-\beta-\beta}-m_0c^2S_{pq}^{-\beta-\beta}\big)C_{pq}^{-\beta}=\epsilon_p^{-\beta}S_{pq}^{-\beta-\beta}C_{pq}^{-\beta}. \tag{B2b}$$

Here, by subtracting the rest mass and using Eq. (B2b) to express $C_{pq}^{-\beta}$,

$$C_{pq}^{-\beta}=c\big\{\big(\epsilon_p^{-\beta}+2m_0c^2\big)S_{pq}^{-\beta-\beta}-V_{pq}^{-\beta-\beta}\big\}^{-1}\times T_{pq}^{-\beta\beta}C_{pq}^{\beta}, \tag{B3}$$

Eq. (B2a) is written as

$$\big\{V_{pq}^{\beta\beta}+c^2T_{pq}^{\beta-\beta}\big[\big(\epsilon_p^{-\beta}+2m_0c^2\big)S_{pq}^{-\beta-\beta}-V_{pq}^{-\beta-\beta}\big]^{-1}T_{pq}^{-\beta\beta}\big\}C_{pq}^{\beta}=\epsilon_p^{\beta}S_{pq}^{\beta\beta}C_{pq}^{\beta}. \tag{B4}$$

Taking into account the nonrelativistic limit ($c\rightarrow\infty$) in Eq. (B4) and simplifying the expression, the following relation is finally obtained:

$$\left\{V_{pq}^{\beta\beta}+\beta\frac{1}{2m_0}T_{pq}^{\beta-\beta}\big[S_{pq}^{-\beta-\beta}\big]^{-1}T_{pq}^{-\beta\beta}\right\}=\epsilon_p^{\beta}S_{pq}^{\beta\beta}C_{pq}^{\beta}. \tag{B5}$$

The second term on the left-hand side of Eq. (B5) has thus become a matrix representation of the nonrelativistic kinetic energy operator,

$$K_{pq}^{\beta\beta}=\beta\frac{1}{2m_0}T_{pq}^{\beta-\beta}\big[S_{pq}^{-\beta-\beta}\big]^{-1}T_{pq}^{-\beta\beta}, \tag{B6}$$

where $T_{pq}^{\beta-\beta}=T_{pq}^{-\beta\beta\dagger}$ and $\epsilon_p^{\beta},\beta=\pm1$ represent the electronic and positronic energy of solutions, respectively.

APPENDIX C: THE EVALUATION OF NONRELATIVISTIC MOLECULAR INTEGRALS

The corresponding nonrelativistic molecular integrals in the solution of the Dirac equation in explicit forms are given here by the following formulas [68].

For two-center overlap,

$$S_{nlm_l,n'l'm_{l'}}(\zeta_A,\zeta_B,\vec{R}_{AB})=\sum_{\nu=0}^{\min(l,l')}T_{lm_l,l'm_{l'}}^{\nu*}(\Theta,\Phi)S_{nl\nu,n'l'\nu}(\zeta_A,\zeta_B,\vec{R}_{AB}), \tag{C1}$$

$$S_{nl\nu,n'l'\nu}(\zeta_A,\zeta_B,\vec{R}_{AB})=\sum_{a=0}^{l}\sum_{b=\nu}^{l'}\sum_{c=0}^{a+b}g_{ab}^{c}(l\nu,l'\nu)\mathcal{P}_{n-a,n'-b,0}^{0,c}\left[0,\frac{R}{2}(\zeta_A+\zeta_B),\frac{R}{2}(\zeta_A-\zeta_B)\right], \tag{C2}$$

with $T_{lm_l,l'm_{l'}}^{\nu}$ rotated-angular functions [77],

$$T_{lm_l,l'm_{l'}}^{\nu}(\Theta,\Phi)=\sum_{L=|l-l'|}^{l+l'}T_{lm_l,l'm_{l'}}^{\nu L}Y_{LM}(\Theta,\Phi), \tag{C3}$$

$$T_{lm_l,l'm_{l'}}^{\nu L}=\frac{2}{1+\delta_{\nu0}}C_{-m_lm_{l'}M}^{ll'L}C_{-\nu\nu0}^{ll'L}\left(\frac{4\pi}{2L+1}\right), \tag{C4}$$

where the quantities C are the Clebsch-Gordan coefficients, $M=-m_l+m_{l'}$, and nuclear attraction integrals,

$$V_{nlm_l,n'l'm_{l'}}(\zeta_A,\zeta_A',\vec{R}_{AB})=\sum_{LM}\sqrt{\frac{4\pi}{2L+1}}C^{L|M|}(lm,l'm')R_{nn'}^{L}(\zeta_A,\zeta_A',R_{AB})Y_{LM}^{*}(\theta_{R_{AB}},\vartheta_{R_{AB}}). \tag{C5}$$

The relativistic molecular auxiliary functions $\mathcal{P}^{N_1,q}_{N_2N_3N_4}(\rho_1,\rho_2,\rho_3)$ [69] in prolate spheroidal coordinates and definitions for the Gaunt and g^c_{ab} coefficients [78,79] occurring in overlap and nuclear attraction integrals are given as follows:

$$\mathcal{P}^{N_1,q}_{N_2N_3N_4}(\rho_1,\rho_2,\rho_3) = \frac{\rho_1^{N_1}}{(N_4-N_1)_{N_1}} \int_1^\infty \int_{-1}^1 (\xi\nu)^q(\xi+\nu)^{N_2}(\xi-\nu)^{N_3} P[N_4-N_1,\rho_1(\xi+\nu)] e^{-\rho_2\xi-\rho_3\nu} d\xi d\nu, \tag{C6}$$

where $(a)_n$ is the Pochhammer symbol, $P[\alpha,x]$ is the normalized incomplete gamma function [41],

$$P[\alpha,x] = \frac{\gamma(\alpha,x)}{\Gamma[\alpha]}, \tag{C7}$$

with $\Gamma[\alpha]$, and $\gamma(\alpha,x)$ are the complete and lower incomplete gamma functions, respectively.

The Gaunt and g^c_{ab} coefficients are defined as

$$C^{L|M|}(lm_l;l'm'_l) = \int_0^\pi \int_0^{2\pi} Y^*_{l|m_l|}(\theta,\vartheta) Y_{l'|m_{l'}|}(\theta,\vartheta) Y_{L|m_l-m_{l'}|}(\theta,\vartheta) \sin\theta d\theta d\vartheta, \tag{C8}$$

$$Y_{l|m_l|}(\theta,\vartheta) = \frac{1}{2\pi}\mathcal{P}_{l|m_l|}(\cos\theta) e^{im_l\vartheta}, \tag{C9}$$

where $\mathcal{P}_{lm_l}(x)$ is the associated Legendre function of the first kind [41], and

$$g^c_{ab}(l\nu,l'\nu) = g^0_{ab}(l\nu,l'\nu) F_q(a+\nu,b-\nu), \tag{C10}$$

$$g^0_{ab}(l\nu,l'\nu) = \sum_{s=0}^{\nu}(-1)^s F_s(\nu) D^{l\nu}_{a+2\nu-2s} D^{l'\nu}_b, \tag{C11}$$

$$D^{l\nu}_b = \frac{1}{2^l}(-1)^{(l-b)/2}\left[\frac{2l+1}{2}\frac{F_l(l+\nu)}{F_\nu(l)}\right]^{1/2} F_{(l-b)/2}(l) F_{b-\nu}(l+b), \tag{C12}$$

where the quantities $F_s(N,N')$ are the generalized binomial coefficients and are given as

$$F_s(N,N') = \sum_{s'}(-1)^{s'} F_{s-s'}(N) F_{s'}(N'), \tag{C13}$$

with $\frac{1}{2}[(s-N)+|s-N|] \leqslant s' \leqslant \min(s,N)$, and $F_s(N)$ are binomial coefficients indexed by N and s usually written as $\binom{N}{s}$, respectively.

Finally, taking into consideration

$$\frac{1}{r_{21}} = \sum_{LM}\left(\frac{4\pi}{2L+1}\right)\left(\frac{r^L_<}{r^{L+1}_>}\right) Y_{LM}(\theta_1,\vartheta_1) Y^*_{LM}(\theta_2,\vartheta_2), \tag{C14}$$

the single-center potential $R^L_{nn'}(\zeta_A,\zeta'_A,R_{AB})$ arising in Eq. (C5) is obtained as

$$R^{\beta\beta';L}_{n\kappa,n'\kappa'}(\zeta_A,\zeta'_A,R_{AB}) = (2\overline{\zeta_A})\Gamma[n+n'+L+1]\frac{1}{(2\overline{\zeta_A}R_{AB})^{L+1}} \times \left\{P[n+n'+L+1,2\overline{\zeta_A}R_{AB}] + \frac{(2\overline{\zeta_A}R_{AB})^{2L+1}}{(n+n'-L)_{2L+1}} Q[n+n'-L,2\overline{\zeta_A}R_{AB}]\right\}, \tag{C15}$$

where $Q[\alpha,x]$ is the normalized complementary incomplete gamma function,

$$Q[\alpha,x] = \frac{\Gamma(\alpha,x)}{\Gamma[\alpha]}, \tag{C16}$$

and $\overline{\zeta_A} = \zeta_A + \zeta'_A$.

Note that the expressions given above for molecular integrals can easily be calculated through the numerical global-adaptive method with the Gauss-Kronrod numerical integration extension used in [68–70].

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[1] P. A. M. Dirac, *Principles of Quantum Mechanics* (Oxford University Press, Oxford, 1978).

[2] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[3] Ts. Tsogbayar and V. I. Korobov, J. Chem. Phys. **125**, 024308 (2006).

[4] Choon-Lin Ho, Ann. Phys. **321**, 2170 (2006).

[5] W. H. E. Schwarz and H. Wallmeier, Mol. Phys. **46**, 1045 (1982).

[6] W. H. E. Schwarz and E. Wechsel-Trakowski, Chem. Phys. Lett. **85**, 94 (1982).

[7] W. Kutzelnigg, Chem. Phys. **395**, 16 (2012).

[8] I. P. Grant, J. Phys. B **43**, 074033 (2010).
[9] Y. S. Lee and A. P. McLean, J. Chem. Phys. **76**, 735 (1982).
[10] R. E. Stanton and S. Havriliak, J. Chem. Phys. **81**, 1910 (1984).
[11] I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules* (Springer, New York, 2007).
[12] K. G. Dyall, Chem. Phys. **395**, 35 (2012).
[13] M. J. Esteban and É. Séré, Commun. Math. Phys. **203**, 499 (1999).
[14] M. Lewin and É. Séré, in *Many-Electron Approaches in Physics, Chemistry and Mathematics*, edited by V. Bach and L. D. Site (Oxford University Press, Oxford, 2014).
[15] M. Lewin and É. Séré, Proc. London Math. Soc. **100**, 864 (2010).
[16] L. Boulton, Appl. Num. Math. **99**, 1 (2016).
[17] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
[18] Yong-Ki Kim, Phys. Rev. **154**, 17 (1967).
[19] S. F. Boys, Proc. R. Soc. London A **200**, 542 (1950).
[20] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[21] I. Pomeranchuk and J. Smorodinsky, J. Phys. USSR **9**, 97 (1945).
[22] Y. Ishikawa and R. Baretty, Chem. Phys. Lett. **121**, 130 (1985).
[23] W. Greiner, B. Müller, and J. Rafelski, *Quantum Electrodynamics of Strong Fields* (Springer-Verlag, Berlin, 1985).
[24] A. E. Shabad, J. Phys. A **38**, 7419 (2005).
[25] B. L. Voronov, D. M. Gitman, and I. V. Tyutin, Theor. Math. Phys. **150**, 34 (2007).
[26] D. M. Gitman, A. D. Levin, I. V. Tyutin, and B. L. Voronov, Phys. Scr. **87**, 038104 (2013).
[27] P. Schwerdtfeger, L. F. Pašteka, A. Punnett, and P. Bowman, Nucl. Phys. A **944**, 551 (2015).
[28] Y. Ishikawa and H. M. Quiney, Int. J. Quant. Chem.: Quant. Chem. Symp. **32**, 523 (1987).
[29] Y. Ishikawa and H. Sekino, Chem. Phys. Lett. **160**, 206 (1989).
[30] G. L. Malli, A. B. F. Da Silva, and Y. Ishikawa, Can. J. Chem. **70**, 1822 (1992).
[31] T. Kato, Commun. Pure. Appl. Math. **10**, 151 (1957).
[32] S. Agmon, Lect. Notes Math. **1159**, 1 (1985).
[33] G. A. Mourou, T. Tajima, and S. V. Bulanov, Rev. Mod. Phys. **78**, 309 (2006).
[34] S. Selsto, E. Lindroth, and J. Bengtsson, Phys. Rev. A **79**, 043418 (2009).
[35] R. Pohl, R. Gilman, G. A. Miller, and K. Pachucki, Annu. Rev. Nucl. Part. Sci. **63**, 175 (2013).
[36] K. Jungmann, Z. Phys. C **56**, S59 (1992).
[37] H. M. Quiney, I. P. Grant, and S. Wilson, in *On the Relativistic Many-Body Perturbation Theory of Atomic and Molecular Electronic Structure*, Lecture Notes in Quantum Chemistry, edited by U. Kaldor, Vol. 52, (Springer-Verlag, Berlin, 1989), pp. 307–344.
[38] I. P. Grant and H. M. Quiney, Phys. Rev. A **62**, 022508 (2000).
[39] C. J. Bostock, J. Phys. B **44**, 083001 (2011).
[40] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-relativistic Theory*, 3rd ed. (Pergamon, Oxford, 1977).
[41] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1972).
[42] P. J. Olver, *Complex Analysis and Conformal Mapping*, http://www.math.umn.edu/~olver/ (unpublished).
[43] E. J. Weniger, J. Phys. A **41**, 425207 (2008).
[44] E. J. Weniger, J. Math. Chem. **50**, 17 (2012).
[45] H. M. Quiney, in *Handbook of Molecular Physics and Quantum Chemistry*, Molecular Electronic Structure, Vol. 2, edited by S. Wilson (Wiley, Chichester, 2003), pp. 423–443.
[46] R. Szmytkowski, J. Math. Chem. **42**, 397 (2007).
[47] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970).
[48] E. O. Steinborn and K. Ruedenberg, Adv. Quantum Chem. **7**, 1 (1973).
[49] H. M. Quiney, P. Belanzoni, and A. Sgamellotti, Theor. Chem. Acc. **108**, 113 (2002).
[50] L. Belpassi, F. Tarantelli, A. Sgamellotti, and H. M. Quiney, Phys. Rev. B **77**, 233403 (2008).
[51] J. M. Leclercq, Phys. Rev. A **1**, 1358 (1970).
[52] H. M. Quiney, I. P. Grant, and S. Wilson, J. Phys. B **20**, 1413 (1987).
[53] K. Koc and Y. Ishikawa, Phys. Rev. A **49**, 794 (1994).
[54] H. M. Quiney, H. Skaane, and I. P. Grant, J. Phys. B **30**, L829 (1997).
[55] H. M. Quiney, H. Skaane, and I. P. Grant, Adv. Quantum Chem. **32**, 1 (1998).
[56] T. Saue, K. Faegri, and O. Gropen, Chem. Phys. Lett. **263**, 360 (1996).
[57] T. Saue, K. Faegri, T. Helgaker, and O. Gropen, Mol. Phys. **91**, 937 (1997).
[58] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two- Electron Atoms* (Springer, Berlin, 1957).
[59] L. Laaksonen and I. P. Grant, Chem. Phys. Lett. **109**, 485 (1984).
[60] L. Yang, D. Heinemann, and D. Kolb, Chem. Phys. Lett. **178**, 213 (1991).
[61] H. Yu, A. D. Bandrauk, and V. Sonnad, Chem. Phys. Lett. **222**, 387 (1994).
[62] S. A. Alexander and R. L. Coldwell, Phys. Rev. E **60**, 3374 (1999).
[63] O. Kullie and D. Kolb, Eur. Phys. J. D **17**, 167 (2001).
[64] O. Kullie and D. Kolb, J. Phys. B **36**, 4361 (2003).
[65] A. Ishikawa, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **128**, 124103 (2008).
[66] A. N. Artemyev, A. Surzhykov, P. Indelicato, G. Plunien, and Th. Stöhlker, J. Phys. B **43**, 235207 (2010).
[67] F. Fillion-Gourdeau, E. Lorin, and A. D. Bandrauk, Phys. Rev. A **85**, 022506 (2012).
[68] A. Bağcı and P. E. Hoggan, Phys. Rev. E **89**, 053307 (2014).
[69] A. Bağcı and P. E. Hoggan, Phys. Rev. E **91**, 023303 (2015).
[70] A. Bağcı and P. E. Hoggan, Phys. Rev. E **92**, 043301 (2015).
[71] Computer code MATHEMATICA (Wolfram Research, Inc., Mathematica, Champaign, IL, 2016), https://www.wolfram.com/mathematica/.
[72] S. Wolfram, *The Mathematica Book*, 5th ed. (Wolfram Media, Champaign, IL, 2003).
[73] M. J. D. Powell, Comput. J. **7**, 155 (1964).
[74] P. J. Mohr, B. N. Taylor, and D. B. Newell, *The 2014 CODATA Recommended Values of the Fundamental Physical Constants* (National Institute of Standards and Technology, Gaithersburg, MD, 2015), http://physics.nist.gov/constants.
[75] J. Reinhardt and W. Greiner, Rep. Prog. Phys. **40**, 219 (1977).
[76] W. Greiner, *Relativistic Quantum Mechanics: Wave Equations* (Springer, Berlin, 2000).
[77] I. I. Guseinov, J. Math. Chem. **49**, 1011 (2011).
[78] I. I. Guseinov, J. Phys. B **3**, 1399 (1970).
[79] I. I. Guseinov, J. Mol. Struct., Theochem. **343**, 173 (1995).