PHYSICAL REVIEW E VOLUME 59, NUMBER 2 FEBRUARY 1999

Addition theorem of Slater-type orbitals: Application to $H_2{}^+$ in a strong magnetic field

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(Received 22 September 1997; revised manuscript received 26 March 1998)

The **C**-matrix representation of the two-range addition theorem of Slater-type functions (STFs) proved to be very useful especially when using a computer algebra system. However, for intensive numerical work it was found advantageous to use the **G**- (or **T**-) matrix representation for the σ part of STFs while the remaining term is expanded with the help of the addition theorem of solid spherical harmonics. Two major advantages are to be related to this procedure. On the one hand, the new **C** matrices are symmetric and most important can be generated recursively. On the other hand, this procedure allows one to generalize and to unify the previous **E**- and **F**-matrix expansions. Indeed, the new **T**-matrix form allows one to avoid the calculation of **C**-matrix elements and much more important to use a recursive scheme in order to generate their elements. As an application of these formulas, we address in the last part of this work the study of the electronic structure of $H_2{}^+$ when subjected to a strong magnetic field. Our calculation shows that the expansion in terms of spherical harmonics (i.e., STFs) becomes slowly convergent for large values of the magnetic field.
[S1063-651X(98)15310-2]

PACS number(s): 02.70.−c, 32.60.+t

I. INTRODUCTION

Slater-type functions (STFs) are known to be mathematically well suited for a good description of atomic and molecular electron densities. However, during the first decades of quantum chemistry their use was limited to very simple molecules owing to the difficulties inherent to the evaluation of the so-called multicenter integrals. Since then, many efforts have been made to elaborate efficient numerical procedures in order to evaluate such integrals. Although limited to linear molecules, the ALCHEMY program [1] was probably the best example of success in using STFs to model complicated molecular systems. In fact, ALCHEMY might be considered as the very first step towards a more sophisticated program dealing with chemical systems of arbitrary geometries. Needless to say, that a generalization of ALCHEMY is not an easy task because one first needs to break through the notorious multicenter integrals problem. For such a purpose, two main methods were thoroughly investigated, namely, the addition-theorem-based methods [2–21] and those using integral transforms [22–32] but so far none of these has really taken the lead. The oldest of these methods is, probably, due to Barnett and Coulson [3] who represent the off-center STF by an infinite multipolar expansion. Perhaps, the main feature of such a series is the form of its Fourier coefficients which are functionals of the electron variable r and have two different analytical forms according to the values of r. This procedure is therefore known as the two-range expansion method. Over the years, many variations of this approach were investigated. Of course, the mathematics leading to these variations is the same as that used by Barnett and Coulson but the original part of each work essentially resides in the manner of representing and computing (when necessary) the Fourier coefficients which we will call Barnett-Coulson–Löwdin functions (BCLFs). As a matter of fact two main representations emerged, namely, the analytical and the numerical way. In the first approach, multicenter integrals are evaluated analytically which implicitly requires an analytic representation of BCLFs. Conversely, the second approach uses numerical integration techniques to deal with multicenter integrals and hence the manner in which BCLFs are represented does not matter as long as this representation yields a fast and numerically stable computational procedure. The above mentioned methods could also be mixed together to obtain what is commonly known as a seminumerical approach in which certain integrals are evaluated analytically while for some others the numerical technique is preferred.

The **C**-matrix formulation of the two-range addition theorem of STFs [33] was proposed with a view to obtaining analytical representations of multicenter integrals. Indeed, since **C**-matrix elements are integers such an approach proved to be very useful when implemented within a computer algebra system (using integer arithmetics) [34,35]. However, the original formulation had two major limitations. On the one hand, it was derived for linear systems lying on the **Z** axis and on the other hand it turned out that some important mathematical results regarding **C** matrices were difficult to establish within such a formulation. Accordingly, the first part of this work proposes a rederivation of the **C**-matrix representation of the addition theorem of STFs. It is shown that by expanding the σ part, $|\mathbf{r}-\mathbf{a}|^{n-l-1}\exp(-\zeta|\mathbf{r}-\mathbf{a}|)$, and the angular term, $|\mathbf{r}-\mathbf{a}|^{l}Y_l^m(\theta,\varphi)$, of a STF separately makes it possible to obtain the expression of **C** matrices in a very straightforward manner. The usefulness of this approach is, then, illustrated by establishing the limits of the indices defining **C** matrices in a much more simple way than that of Rashid [9] and Suzuki [36]. In the second part, we show another of its advantageous aspects by rederiving the series representation of BCLFs which in contrast to the previous one involves only one matrix (called **T**) whose elements can be computed recursively. Another noteworthy

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advantage of this procedure is that a polynomial approximation of BCLFs may be constructed with the help of the so-called Lanczos-τ method which also allows one to calculate the deviation from the exact result in advance. The third part of this work is finally devoted to calculating the ground-state energy of H_2^+ when experiencing a strong to superstrong magnetic field. For such a purpose, we opted to use an atomic basis set in which all of the STFs have the same screening constants (to facilitate the optimization work).

II. BARNETT-COULSON–LÖWDIN FUNCTIONS: AN OUTLINE

A. Introduction to Barnett-Coulson–Löwdin functions

In an early work devoted to the elaboration of a general algorithm for the evaluation of multicenter integrals over STFs, Barnett and Coulson [3] proposed to use an addition theorem in order to separate the integration variables from the parameters related to the geometrical structure of the molecule. Strictly speaking, this addition theorem allowed the authors to expand the σ part of a STF in the following way:

$$|\mathbf{r}-\mathbf{a}|^{n-1}\exp(-\beta|\mathbf{r}-\mathbf{a}|)=\sum_{\lambda=0}^{+\infty}(2\lambda+1)\,\frac{2\lambda+1}{\sqrt{ar}}\times\zeta_{n,\lambda}(\beta,a,r)P_\lambda\left(\frac{\mathbf{a}\cdot\mathbf{r}}{ar}\right),\tag{1}$$

where $P_n(z)$ represents the standard Legendre polynomials while $\zeta_{n,\lambda}(\beta,a,r)$ is a function that depends only on the Slater exponent β and the modulus of the vectors $\mathbf{r}$ and $\mathbf{a}$. The Barnett-Coulson $\zeta_{m,n}$ functions appeared afterwards in a review paper of Löwdin [4] under the name of α functions. Many authors have, henceforth, referred to these functions as Löwdin α functions. In this work we prefer to call these quantities Barnett-Coulson–Löwdin functions and use the notation $\mathcal{A}^n_{l+1/2}(\beta,a,r)$. In fact Eq. (1) is straightforwardly obtained by differentiating n times (with respect to β) the Gegenbauer addition theorem of the Yukawa potential ([37], p. 107), that is to say, $\exp(-\beta|\mathbf{r}-\mathbf{a}|)/|\mathbf{r}-\mathbf{a}|$. This yields the following definition for BCLFs:

$$\begin{aligned}\mathcal{A}^0_{\lambda+1/2}(\beta,a,r)&=\mathbf{I}_{\lambda+1/2}(\beta\rho_<)\mathbf{K}_{\lambda+1/2}(\beta\rho_>),\\ \mathcal{A}^n_{\lambda+1/2}(\beta,a,r)&=-(\partial/\partial\beta)\mathcal{A}^{n-1}_{\lambda+1/2}(\beta,a,r),\end{aligned}\tag{2}$$

where $\rho_<$ and $\rho_>$ denote min(a,r) and max(a,r), respectively. Here, it should be pointed out that in addition to the above definition, one can find in the literature numerous variations of this definition. Such variations are essentially obtained by including or dropping some multiplication factors.

B. Expansion of the angular part of a STF

In previous work Jones and Weatherford [33] introduced a special representation of BCLFs, the so-called $\mathbf{C}$-matrix representation, which is well adapted for integer arithmetic calculations since the elements of such matrices are integers. In their derivation, the authors simplified the mathematics by assuming the center of the STF on the $\mathbf{Z}$ axis. Obviously, this formalism can easily be generalized to an arbitrary center by including a suitable Wigner rotation matrix. However, in doing so the expression of the $\mathbf{C}$ matrices becomes far more complicated. In the rest of this section, it is our aim to develop the mathematics allowing us to obtain a more convenient $\mathbf{C}$-matrix representation of a general BCLF (2), i.e., corresponding to a STF located on an arbitrary center. For such a purpose, instead of expanding the STF directly over a complete basis set of surface spherical harmonics we prefer using a product of two addition theorems which have the advantage of making a clear distinction between the term which is easy to translate and that which is not. In fact the easier part is obviously the angular term which is expandable according to the following relationship [38]:

$$\begin{aligned}\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a})={}&4\pi(2l+1)!!\\ &\times\sum_{l'=0}^{l}\sum_{m'=-l'}^{l'}\frac{\langle lm|l'm'|l-l'm-m'\rangle}{(2l'+1)!![2(l-l')+1]!!}\\ &\times\mathcal{Y}_{l-l'}^{m-m'}(-\mathbf{a})\mathcal{Y}_{l'}^{m'}(\mathbf{r}).\end{aligned}\tag{3}$$

C. Derivation of a C-matrix representation

Regarding the difficult part, i.e., the σ part of a STF, we use the expansion of Eq. (1). Thus, starting with the Gegenbauer expansion of the Yukawa potential ([37], p. 107) in which the modified Bessel functions are expanded according to Ref. [37] (p. 72), one obtains after some algebra the following $\mathbf{C}$-matrix representation of the zeroth order BCLF:

$$\begin{aligned}\frac{\mathcal{A}^0_{\lambda+1/2}(\zeta,a,r)}{\sqrt{ar}}={}&(-1)^\lambda\,\frac{\zeta}{2}\sum_{i=0}^{\lambda}\sum_{j=0}^{\lambda}\mathbf{C}^0_\lambda(i,j)(\zeta\rho_<)^{i-\lambda-1}\\ &\times(\zeta\rho_>)^{j-\lambda-1}H_i(\zeta,a,r),\end{aligned}\tag{4}$$

where the function $H_i(\zeta,a,r)$ is defined as

$$H_i(\zeta,a,r)=\exp(-\zeta\rho_>)[(-1)^i\,\exp(\zeta\rho_<)-\exp(-\zeta\rho_<)],\tag{5}$$

where the $\mathbf{C}$ matrices corresponding to this are as follows:

$$\mathbf{C}^0_\lambda(i,j)=\frac{(\lambda-i)!}{2^{\lambda-i}}\,\frac{(\lambda-j)!}{2^{\lambda-j}}\binom{\lambda}{i}\binom{2\lambda-i}{\lambda}\binom{\lambda}{j}\binom{2\lambda-j}{\lambda}.\tag{6}$$

From the above definition it could be seen that the elements of the zeroth order $\mathbf{C}$ matrix are integers. To obtain a similar representation for the nth order BCLF, it suffices to differentiate n times both sides of Eq. (4) with respect to ζ. This yields

$$\begin{aligned}\frac{\mathcal{A}^n_{\lambda+1/2}(\zeta,a,r)}{\sqrt{ar}}={}&\frac{(-1)^\lambda}{2\zeta^{n-1}}\sum_{i=0}^{\lambda}\sum_{j=0}^{\lambda}\sum_{p=0}^{n}\sum_{q=0}^{p}\binom{n}{p}\binom{p}{q}\\ &\times(2\lambda-i-j+1)_{n-p}\mathbf{C}^0_\lambda(i,j)\\ &\times(\zeta\rho_<)^{i+q-\lambda-1}(\zeta\rho_>)^{j+p-q-\lambda-1}\\ &\times H_{i+q}(\zeta,a,r),\end{aligned}\tag{7}$$

where the $(a)_n$ represents the Pochhammer symbol. Setting $\mu=i+q$ and $\nu=j+p-q$ and changing the summation limits one obtains after some simple algebra

$$\frac{\mathcal{A}^n_{\lambda+1/2}(\zeta,a,r)}{\sqrt{ar}}=\sum_{\mu=0}^{\lambda+n}\sum_{\nu=0}^{\lambda+n}\mathbf{C}^n_\lambda(\mu,\nu)(\zeta\rho_<)^{\mu-\lambda-1}\times(\zeta\rho_>)^{\nu-\lambda-1}H_\mu(\zeta,a,r), \tag{8}$$

where the matrix $\mathbf{C}^n_\lambda$ involved in this expression is connected to that of order zero according to

$$\mathbf{C}^n_\lambda(i,j)=\sum_{p=0}^{n}\sum_{q=\max(0,i-\lambda,p-j)}^{\min(p,i,\lambda+p-j)}\binom{n}{p}\binom{p}{q}\times(2\lambda-i-j+p+1)_{n-q}\mathbf{C}^0_\lambda(i-q,j-p+q). \tag{9}$$

Here it should be pointed out that the above $\mathbf{C}$-matrix representation of BCLFs (which in fact corresponds to the expansion of an *s*-type STF) is numerically equivalent to that given by Jones and Weatherford [39] in the sense that the values generated with Eq. (9) are identical to those obtained with the definition of Refs. [33,39]. However, the present approach reveals certain numerical properties that can be advantageous when addressing computational work. Indeed, Eq. (9) shows that our $\mathbf{C}$ matrices are not only symmetrical but more importantly their elements may be computed from those of $\mathbf{C}^0_\lambda$ which in turn satisfy a very simple recurrence relation [cf. Eq. (6)]. Moreover, the present representation permits one to prove several mathematical properties almost effortlessly which in the framework of Sharma's [6] approach would require tedious algebraic work. As a first instance, let us show that for $i>n+l+\lambda$ the elements of the general $\mathbf{C}(i,j)$ matrices (as defined in Ref. [33]) vanish. This was proved differently by Rashid [9] and by Suzuki [36] using a similar strategy, namely, performing several summations by means of suitable combinations of the addition and multiplication theorems of the binomial coefficients. In our case we can arrive at the same result without any further calculations by a simple examination of the highest powers of the terms (ζa) and (ζr). Indeed working under the same conditions as these authors, i.e., assuming vector $\mathbf{a}$ on the $\mathbf{Z}$ axis the addition theorem of Eq. (3) takes the following form:

$$\mathcal{Y}^m_l(\mathbf{r}-\mathbf{a})=4\pi(2l+1)!!\sum_{l'=0}^{l-|m|}(-1)^{l-l'-|m|}\times\frac{\langle lm|l'+|m|m|l-l'-|m|0\rangle}{[2(l'+|m|)+1]!![2(l-l'-|m|)+1]!!}\times a^{l-l'-|m|}r^{l'+|m|}\mathcal{Y}^m_{l'+|m|}(\mathbf{r}). \tag{10}$$

Thus multiplying the above expression with that of Eq. (8), in which n is first replaced by $n-l$, and collecting the powers of (ζa) and (ζr) one obtains a product of the form $(\zeta a)^{\mu-\lambda-1+l-l'-|m|}(\zeta r)^{\nu-\lambda-1+l'+|m|}$. Here, it should be emphasized that since our $\mathbf{C}$ matrices are symmetrical it does not matter which of the variables $\rho_<$ and $\rho_>$ in Eq. (8) corresponds to a and r. In the notation of Refs. [9,33,36] the powers of (ζa) and (ζr) were, respectively, written as $i-l-\lambda-1$ and $j-l-\lambda-1$. Thus comparison of these numbers to those defined above yields the following relationships:

$$i=\mu+2l-l'-|m|,\quad\text{and}\quad j=\nu-l+l'+|m|. \tag{11}$$

From these equations, obtaining the upper limits of i and j is straightforward since use of simple algebra yields $\max(i)=n+l+\lambda$ and $\max(j)=n+\lambda$. This clearly demonstrates the flexibility provided by separating the σ part and the angular part of a STF. Furthermore, using the same strategy it can also be shown that in the case of arbitrary $\mathbf{a}$, i.e., not lying on the $\mathbf{Z}$ axis, the summation limit derived above for i is no longer valid.

III. SERIES REPRESENTATION OF BCLFs

In computing molecular multicenter integrals, it may be necessary to compute numerical values of BCLFs, $\mathcal{A}^n_\nu(\zeta,a,r)$, with large orders ν. It is, therefore, important to elaborate numerically stable representations of such functions. According to previous work [21], it was shown that use of closed analytical forms of modified Bessel functions in the definition of BCLFs (2) ultimately lead to the $\mathbf{C}$-matrix formalism, proposed by Jones and Weatherford [33]. However, in spite of its analytical interest, such an approach is not well adapted for intensive numerical computation with double precision coding since the elements of $\mathbf{C}$ matrices increase in size very rapidly, making the final results often inaccurate. Fortunately, this aspect of the $\mathbf{C}$-matrix formulation may be overcome by means of two different strategies. Indeed, if very small basis sets are considered, use of the $\mathbf{C}$-matrix formulation for numerical purposes can be made possible by means of a high-precision arithmetic. However, as pointed out by Kravchenko and co-workers [40–42] general-purpose programs such as MAPLE or MATHEMATICA will certainly be very slow and only specialized packages will offer the best performances. In addition to the high-quality results presented by these authors, the most significant conclusion is that high-precision arithmetic does not lead to a catastrophic loss of speed when the basic operations are performed by means of special algorithms [42].

As an alternative to high-precision arithmetic, Jones [43] expanded BCLFs in the form of a Taylor series which led to the so-called $\mathbf{E}$- and $\mathbf{F}$-matrix expansion. $\mathbf{E}$ matrices are used for numerical computations inside the sphere of radius $r=a$ while $\mathbf{F}$ matrices are used outside this sphere. The rest of this section introduces a generalization of this approach in which only one matrix is involved. To do so, let us substitute for the modified Bessel functions $\mathbf{I}_{l+1/2}(\zeta\rho_<)$ and $\mathbf{K}_{l+1/2}(\zeta\rho_>)$ involved in the definition of BCLFs (2), respectively, the series expansion given in Ref. [37] (p. 66) and the closed analytical expression of Ref. [37] (p. 72). Hence, simplifying the result following from the nth derivative with respect to ζ, one obtains

$$\mathcal{A}^n_{l+1/2}(\zeta,a,r)=(-1)^n\frac{2}{\zeta^n}\left(\frac{\rho_<}{\rho_>}\right)^{l+1/2}\exp(-\zeta\rho_>)\times\sum_{p=0}^{+\infty}\sum_{s=\max(0,n-2p)}^{l+n}\mathbf{T}^{l,n}_{p,s}(\zeta\rho_<)^{2p}(\zeta\rho_>)^s, \tag{12}$$

where the matrix element $\mathbf{T}^{l,n}_{p,s}$ is defined as

$$\mathbf{T}^{l,n}_{p,s}=n!\,\frac{(l+p+1)!}{p!(2l+2p+2)!}\,\frac{(-1)^s}{(2p-n+s)!}\times\left[\sum_{q=q_{\min}}^{q_{\max}}(-1)^q\,\frac{2^q(2l-q)!}{q!(l-q)!}\,\frac{(2p+q)!}{(s-q)!(n-s+q)!}\right], \tag{13}$$

with $q_{\min}=\max(0,s-n)$ and $q_{\max}=\min(l,s)$.

Here, it should be stressed that our **T**-matrix expansion exhibits at least two advantages. The first is the uniqueness of the definition of their elements since according to Eq. (12), the same **T** matrix is used in both regions of the space, i.e., inside and outside the sphere $r=a$. Such an expansion may hence be considered as a unified series representation of BCLFs. The second advantage related to the above expansion is the possibility of using Eq. (13) to generate efficiently **T**-matrix elements. As a matter of fact such a calculation may be carried out following two ways. In the first approach, we start by rewriting the definition of **T**-matrix elements (13) as follows:

$$\mathbf{T}^{l,n}_{p,s}=(-1)^s u_p\sum_{q=q_{\min}}^{q_{\max}}\binom{n}{s-q}v_q w_q, \tag{14}$$

where the terms u_p, v_q, and w_q are defined according to

$$u_p=\frac{(2l)!}{l!}\,\frac{(2p)!(l+p+1)!}{p!(2l+2p+2)!},\quad v_q=\frac{l!}{(2l)!}\,2^q\,\frac{(2l-q)!}{q!(l-q)!}, \tag{15}$$

$$w_q=\frac{(2p)!}{(2p-n+s)!}\,(2p+q)!.$$

From a numerical viewpoint, it is clear that the above definitions lend themselves to a recursive evaluation but more importantly they also allow the internal computer rounding error to be easily controlled since no large number is generated.

The second approach we are proposing for the evaluation of **T**-matrix elements is founded on a completely recursive algorithm. Indeed, the derivative of the series representation of the function $\mathcal{A}^n_\nu(\zeta,a,r)$ given by Eq. (12) with respect to ζ yields the following recurrence relation:

$$\mathbf{T}^{l,n+1}_{p,s}=(2p+s-n)\mathbf{T}^{l,n}_{p,s}-\mathbf{T}^{l,n}_{p,s-1}. \tag{16}$$

To initialize the numerical procedure, it was found convenient to start with the zeroth order **T** matrix, i.e., $\mathbf{T}^{l,0}$, since its elements are defined explicitly by

$$\mathbf{T}^{l,0}_{p,s}=\frac{(l+p+1)!}{p!(2l+2p+2)!}\,\frac{2^s(2l-s)!}{s!(l-s)!}. \tag{17}$$

Moreover, the above ratio may easily be computed using a simple recursive procedure, since the elements $\mathbf{T}^{l,0}_{p+1,s}$ and $\mathbf{T}^{l,0}_{p,s+1}$ may be related to $\mathbf{T}^{l,0}_{p,s}$ by means of simple relationships. The first few **T** matrices presented in Table I have been obtained with the help of a simple FORTRAN program using the recurrence relation (16).

Thus far, a general **T**-matrix expansion was derived after substituting a Taylor series for the modified Bessel function $\mathbf{I}_\nu(\zeta\rho_<)$ occurring in the definition of BCLFs. With respect to computational efficiency it would, however, be of interest to derive an alternative expansion which is valid only within a finite range of the form $[0,\tau_{\max}]$. This additional step is mainly motivated by the fact that in most molecular calculations the small values of the argument $\zeta\rho_<$ are frequently encountered in comparison to large values of this argument (in which case the multicenter integral will probably be neglected). In addition to this physical argument, it is well known that despite their tremendous analytical significance, Taylor series are of little use for computational purposes since there exist much more useful expansions generally based on the use of orthogonal polynomials. Indeed, a typical situation with Taylor series is that they converge very rapidly in the neighborhood of the center of expansion while they become poorly convergent as one goes away from this center. Conversely, use of a suitable class of orthogonal polynomials allows the error to be distributed over the entire range, i.e., its magnitude remains approximately the same. In the case of interest use of the so-called Lanczos-τ method allows one to obtain (within a given sphere $r\leq r_{\max}$) a polynomial approximation of BCLFs and in the meantime the upper bound of the deviation from the exact expansion. Accordingly, our starting point will be the differential equation satisfied by the reduced Bessel function $\hat{\iota}_l=\mathbf{I}_{l+1/2}(z)/z^{l+1/2}$ which reads as follows:

$$z^2\hat{\iota}_l''(z)+2(l+1)z\hat{\iota}_l'(z)-z^2\hat{\iota}_l(z)=0,$$

with

$$\hat{\iota}_l(0)=a_0=\frac{1}{2^{l+1/2}\Gamma(l+\frac{3}{2})}. \tag{18}$$

From this equation, it is clear that since $\hat{\iota}_l(z)$ is an even function its series expansion should contain only even powers of the variable, that is to say, $\hat{\iota}_l(z)=\Sigma_q a^{(l)}_{2q}z^{2q}$. Now, if this series is approximated by the first N terms (i.e., a polynomial of degree $2N$), Eq. (18) ultimately leads to the cancellation of all coefficients $\{a^{(l)}_{2q}\}_{q=0,1,\ldots,N}$. In order to avoid this troublesome situation, Lanczos [44] (p. 464) proposed to introduce in the right hand side of the initial differential equation (18) a perturbation term the magnitude of which may be made as small as we please. In the original method of Lanczos and its well-known variation elaborated by Clenshaw the perturbative term is generally written as a linear combination of Tchebyshev polynomials. Note that in further studies of this method other bounded orthogonal polynomials were also used. In the present case we can write

$$z^2\hat{\iota}_l''(z)+2(l+1)z\hat{\iota}_l'(z)-z^2\hat{\iota}_l(z)=\tau T_{2N}\left(\frac{z}{r_{\max}}\right)+\tau' T_{2(N+1)}\left(\frac{z}{r_{\max}}\right), \tag{19}$$

where $T_\nu(z)$ stands for the well-known Tchebyshev polynomial ([37], p. 256) of degree ν while $r_{\max}$ is the upper bound of the range within which the expansion is being elaborated. The parameters τ and τ' are additional unknowns which on

TABLE I. Inverse of the elements of $\mathbf{T}^{l,n}$ matrices computed recursively with the help of the relationship (16).

$$\mathbf{T}^{0,0}=\begin{bmatrix} 1 \\ 6 \\ 120 \\ 5\,040 \\ 362\,880 \\ 39\,916\,800 \end{bmatrix} \qquad \mathbf{T}^{0,1}=\begin{bmatrix} \infty & -1 \\ 3 & -6 \\ 30 & 120 \\ 45\,360 & 362\,880 \\ 3\,991\,680 & -3\,991\,680 \end{bmatrix}$$

$$\mathbf{T}^{2,0}=\begin{bmatrix} 5 & 5 & 15 \\ 70 & 70 & 210 \\ 2\,520 & 2\,520 & 7\,560 \\ 166\,320 & 166\,320 & 498\,960 \end{bmatrix} \qquad \mathbf{T}^{2,1}=\begin{bmatrix} \infty & \infty & -15 & -15 \\ 35 & 35 & 210 & -210 \\ 630 & 630 & 2\,520 & -7\,560 \\ 27\,720 & 27\,720 & 99\,792 & -498\,960 \\ 2\,162\,160 & 2\,162\,160 & 7\,413\,120 & -51\,891\,840 \\ 259\,459\,200 & 259\,459\,200 & 864\,864\,000 & -7\,783\,776\,000 \end{bmatrix}$$

$$\mathbf{T}^{4,0}=\begin{bmatrix} 9 & 9 & 21 & 189 & 945 \\ 198 & 198 & 462 & 2\,079 & 20\,790 \\ 10\,296 & 10\,296 & 24\,024 & 108\,108 & 1\,081\,080 \\ 926\,640 & 926\,640 & 2\,162\,160 & 9\,729\,720 & 97\,297\,200 \\ 126\,023\,040 & 126\,023\,040 & 294\,053\,760 & 1\,323\,241\,920 & 13\,232\,419\,200 \\ 23\,944\,377\,600 & 23\,944\,377\,600 & 55\,870\,214\,400 & 251\,415\,964\,800 & 2\,514\,159\,648\,000 \end{bmatrix}$$

$$\mathbf{T}^{4,1}=\begin{bmatrix} \infty & \infty & -63 & -63 & -315 & -945 \\ 99 & 99 & 1\,386 & 4\,158 & -10\,395 & -20\,790 \\ 2\,574 & 2\,574 & 6\,552 & 216\,216 & -540\,540 & -1\,081\,080 \\ 154\,440 & 154\,440 & 6\,486\,480 & 2\,162\,160 & \infty & -97\,297\,200 \\ 15\,752\,880 & 15\,752\,880 & 882\,161\,280 & 203\,575\,680 & 6\,616\,209\,600 & -13\,232\,419\,200 \\ 2\,394\,437\,760 & 2\,394\,437\,760 & 167\,610\,643\,200 & 29\,578\,348\,800 & 628\,539\,912\,000 & -2\,514\,159\,648\,000 \end{bmatrix}$$

the one hand prevent overdetermination and on the other hand give the accuracy of the polynomial approximation. Indeed, since Tchebyshev polynomials satisfy the inequality $|T_\nu(z)|\leqslant 1$ for any real argument $z\in[-1,1]$, then making use of the Schwartz inequality one obtains

$$\left|\tau T_{2N}\left(\frac{z}{r_{\max}}\right)+\tau' T_{2(N+1)}\left(\frac{z}{r_{\max}}\right)\right|\leqslant|\tau|+|\tau'|. \qquad (20)$$

Now, expanding both sides of the differential equation (19) yields, after some straightforward algebra, the following system:

$$0=\tau+\tau',$$

$$2q(2q+2l+1)a_{2q}^{(l)}-a_{2(q-1)}^{(l)}=\tau c_{2m}^{2N}+\tau' c_{2m}^{2(N+1)},$$

$$m=1,2,...,N \qquad (21)$$

$$a_{2N}^{(l)}=\tau' c_{2(N+1)}^{2(N+1)}=\tau' 2^{2N+1},$$

$$\hat{\iota}_l(0)=1/[2^{l+1/2}\Gamma(l+\tfrac{1}{2})],$$

where c_m^ν represents the coefficient multiplying the mth degree monomial involved in the Tchebyshev polynomial $T_\nu(z)$. For numerical purposes the above system can be solved using essentially two different approaches. The first way and probably the most straightforward is to use a computer algebra system to generate the analytical formulas defining the unknowns $a_{2q}^{(l)}$ as well as τ and τ'. These definitions will obviously be a function of the parameter l. Within the range $z\in[-6,+6]$ used in Table II, the modified Bessel function $\mathbf{I}_{n+1/2}(z)$ is evaluated by means of the following polynomial approximation:

$$\mathbf{I}_{n+1/2}(z)=\frac{a_0}{D(n)}\,z^{n+1/2}\sum_{q=0}^{6} a_{2q}z^{2q},$$

where $D(n)$ has the definition

$$D(n)=n^6+\frac{153}{8}\,n^5+\frac{5021}{32}\,n^4+\frac{437\,763}{640}\,n^3 +\frac{8\,441\,639}{5120}\,n^2+\frac{168\,247\,461}{81\,920}\,n+\frac{334\,678\,851}{327\,680}.$$

Apart from a_0 which is defined by the initial condition [Eq. (18)], all the other coefficients a_{2q} involved in the above polynomial approximation are to be evaluated according to the relationship

$$a_{2q}=\sum_{p=0}^{5} c_p n^p, \quad \text{with } q=1,2,...$$

TABLE II. Lanczos expansion of the reduced Bessel function $\hat{\imath}_n(z)$ for $z \in [-6,+6]$ [cf. Eq. (18)].

Coefficients	a_2	a_4	a_6	a_8	a_{10}	a_{12}
c_0	55 651 869/327 680	1 406 223/163 840	637/196 608	15 951/81 920	13/983 040	1/2 949 120
c_1	469 148/20 480	164 263/20 480	1663/12 288	19/16 384	1/122 880	0
c_2	312 513/2 560	2 965/1 024	31/1 024	1/6 144	0	0
c_3	4 175/128	121/256	1/384	0	0	0
c_4	141/32	1/32	0	0	0	0
c_5	1/4	0	0	0	0	0

where the numerical values of the factors c_p are given in Table II.

The formulas given above may be rewritten in a form suitable for intensive numerical calculation using optimized evaluation schemes, e.g., the Horner algorithm. In fact, if the largest value of l is *a priori* known, the storage of such general formulas becomes unnecessary because for any $\mu \leqslant l-1$ the coefficients $\{a_{2q}^{(\mu)}\}_{0\leqslant q\leqslant N}$ may be determined from those describing $\hat{\imath}_l(z)$ and $\hat{\imath}_{l-1}(z)$, i.e., $\{a_{2q}^{(l)}\}_{0\leqslant q\leqslant N}$ and $\{a_{2q}^{(l-1)}\}_{0\leqslant q\leqslant N}$, thanks to the following three-term recurrence relation:

$$\hat{\imath}_{l-1}(z)=z^2\hat{\imath}_{l+1}(z)+(2l+1)\hat{\imath}_l(z). \tag{22}$$

Clearly from the above equation, it becomes straightforward to derive the relationship connecting the coefficients $a_{2q}^{(l-1)}$ to $a_{2q}^{(l)}$ and $a_{2q}^{(l+1)}$ which reads as follows:

$$\begin{aligned} a_0^{(l-1)}&=(2l+1)a_0^l, \\ a_{2q}^{(l-1)}&=(2l+1)a_{2q}^{(l)}+a_{2q}^{(l+1)}, \quad q=1,2,...,N. \end{aligned} \tag{23}$$

As an alternative to computer algebra, the linear system (21) may also be solved using a more conventional numerical method. In such a case it may be seen that the first of equations (21) yields $\tau=-\tau'$ which allows one to reduce the dimensionality of our system. The coefficients $\{a_{2q}^{(l)}\}_{0\leqslant q\leqslant N}$ are then determined using a backward recursive procedure starting with $a_{2N}^{(l)}$. Of course at the end of this calculation the coefficients under consideration will be a function of τ' which in turn is determined from the initial condition $\hat{\imath}_l(0)$. Note that although large numbers are generated by this procedure, it does not suffer from numerical instabilities since all the intermediate numbers are finally divided by the largest of such numbers. In the Appendix general analytical formulas defining $\{a_{2q}^{(l)}\}_{0\leqslant q\leqslant N}$ and τ' are given.

IV. $H_2{}^+$ IN A STRONG MAGNETIC FIELD

In this section it is our aim to check the accuracy and the usefulness of the approach developed above by applying the analytical results to the very simple molecule $H_2{}^+$ when subjected to a strong magnetic field parallel to its principal axis (assumed to be the **Z** axis). Here, note has to taken that in spite of its simplicity, the study of $H_2{}^+$ still raises very interesting investigations. As a matter of fact, when experiencing strong magnetic fields, the change in the behavior of matter is so complex that up to now most of the theoretical investigations were conducted on a very short list of diatomic molecules (see, for instance, Ref. [45]). On top of this list, we find the hydrogen molecular ion which over the years yielded a wealth of numerical results [46–59].

In the nonrelativistic approximation, the total Hamiltonian describing a spinless $H_2{}^+$ when subjected to a magnetic field **B** may be expressed in the laboratory coordinate system (indicated by capital L) as follows:

$$\hat{\mathbb{H}}_L=\sum_{i=e,a,b}\frac{1}{2m_i}\left[\hat{\mathbf{P}}_{i/L}-\frac{e_i}{c}\mathbf{A}_{i/L}\right]^2+\frac{1}{2}\sum_{j\neq i}\frac{e_ie_j}{|\mathbf{R}_{i/L}-\mathbf{R}_{j/L}|}, \tag{24}$$

where the indices i and j run over the electron (e), and the protons (a) and (b). The variable e_i represents the charge of the ith particle. In atomic units this value is either (-1) or $(+1)$. In addition, for our subsequent calculations the vector potentials $\mathbf{A}_{li}$ are taken in the gauge, making $\boldsymbol{\nabla}\cdot\mathbf{A}_{i/L}=0$.

Following the detailed paper of Khersonskij [51], the above molecular Hamiltonian breaks down into several terms which when using the Born-Oppenheimer (adiabatic) approximation allows one to write for the molecule the following Hamiltonian (in atomic units):

$$\hat{\mathbb{H}}_M=-\frac{1}{2}\nabla_e^2+\frac{\beta}{2}\hat{L}_z+\frac{\beta^2}{8}\rho^2-\frac{1}{R_a}-\frac{1}{R_b}+\frac{1}{R}, \tag{25}$$

where β stands for the ratio B/B_0 in which B_0 represents the reference magnetic field strength $(1\text{ a.u.}=2.350\,54\times10^9\text{ G})$. $\hat{L}_z$ denotes the **Z** component of the angular momentum operator which in spherical coordinates is defined as $\hat{L}_z=-i\hbar\partial/\partial\varphi$. The geometric parameters are explicitly described in Fig. 1.

To solve the Schrödinger equation involving the Hamiltonian (25), we will use the Hartree-Fock variational procedure in which molecular orbitals (MOs) are represented by a linear combination of atomic orbitals (LCAO-MO). Accordingly, the ith MO will be written as

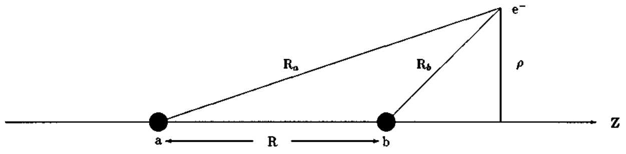

FIG. 1. Coordinate system.

TABLE III. Convergence of the LCAO-MO ionization energy of $1\sigma_g$ as a function of the size of the atomic basis set. The same Slater exponent was used for all AOs.

Basis set[a]	ζ	$R=1$	ζ	$R=2$	ζ	$R=3$	ζ	$R=10$	ζ	$R=20$
$1s$	1.52	0.440 836 5	1.24	0.586 505 0	1.08	0.564 315 7	1.00	0.500 297 5	1.00	0.500 000 0
$2s$, $2p$	1.92	0.451 529 3	1.56	0.602 166 2	1.36	0.576 614 1	1.00	0.500 524 2	1.00	0.500 012 5
$3s$, $3p$	1.92	0.451 662 3	1.80	0.602 238 9	1.64	0.577 073 1	1.00	0.500 561 6	1.00	0.500 014 1
$4s$, $4p$, $3d$	2.12	0.451 768 3	1.84	0.602 600 7	1.60	0.577 532 2	1.00	0.500 574 9	1.00	0.500 014 2
$5s$, $5p$, $4d$	2.32	0.451 781 7	1.88	0.602 625 4	1.36	0.577 538 8	1.04	0.500 576 9	1.00	0.500 014 3
$6s$, $6p$, $5d$, $4f$	2.40	0.451 785 0	2.12	0.602 632 4	1.88	0.577 560 5	1.00	0.500 578 3	1.00	0.500 014 3
Exact[b]		0.451 786 3		0.602 634 2		0.577 562 9		0.500 578 7		0.500 014 3

[a] An atomic basis set of the form $\{As,Bp,Cd\dots\}$ includes the AOs of the form $\{\{1s,2s,\dots,As\},\{2p,3p,\dots,Bp\},\{3d,4d,\dots,Cd\},\dots\}$.

[b] Exact values for binding energies and other expectation values are to be found in Ref. [63].

$$\phi_i=\sum_{\mu=1}^{N} c_{\mu i}\chi_\mu, \tag{26}$$

in which the χ_μ are the AOs. From this definition, it is obvious that AOs should carefully be chosen in order to make the approximate (i.e., variational) solution converge rapidly to the exact wave function. In the free-field case, it is customary to expand MOs in terms of STFs since the latter give a reliable description of the electron densities in all regions of the space and especially in the vicinity of the nuclei and farther away. Within the framework of the LCAO-MO approach, the calculation of the electronic energy of H_2^+ requires the evaluation of two types of integrals:

$$\mathcal{J}_1=\langle\chi_{n_1,l_1,m_1}(\zeta_1\mathbf{R}_a)|\mathcal{O}|\chi_{n_2,l_2,m_2}(\zeta_2\mathbf{R}_a)\rangle,$$

$$\mathcal{J}_2=\langle\chi_{n_1,l_1,m_1}(\zeta_1\mathbf{R}_a)|\mathcal{O}|\chi_{n_1,l_1,m_1}(\zeta_2\mathbf{R}_b)\rangle, \tag{27}$$

where $\mathcal{O}$ represents the kinetic energy operator $-1/2\Delta_a$ or the Coulomb operator $1/\mathbf{R}_a$ or the unity constant. For numerical purposes it may be seen that the basic building block to the above quantities is the overlap integral obtained by setting the operator $\mathcal{O}=1$. Obviously, one-center overlaps are just the Laplace transform of a monomial function of the form R_a^μ. As regards the two-center integrals, combination of the addition theorem (1) with that of Eq. (3) yields after some algebra the following expression:

$$S_{n_1,l_1,m_1}^{n_2,l_2,m_2}(\zeta_1,\zeta_2,\mathbf{b})=\mathcal{N}_1\mathcal{N}_2(4\pi)^2(2l_2+1)!!\sum_{l_2'=0}^{l_2}\sum_{m_2'=-l_2'}^{l_2'}\frac{\langle l_2m_2|l_2'm_2'|l_2-l_2'm_2-m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!}\mathcal{Y}_{l_2-l_2'}^{m_2-m_2'}(-\mathbf{b})$$
$$\times\sum_{\lambda=|l_1-l_2'|}^{l_1+l_2'}{}''\langle l_1m_1|l_2'm_2'|\lambda m_1-m_2'\rangle\langle r^{n_1-1}\exp(-\zeta_1 r)|r^{l_2'}\mathcal{A}_{\lambda+1/2}^{n_2-l_2}(\zeta_2,b,r)/\sqrt{br}\rangle[\mathcal{Y}_\lambda^{m_1-m_2'}(\mathbf{b}/b)]^* \tag{28}$$

in which Σ'' indicates that the summation is performed with steps of 2 and $\langle l_1m_1|l_2m_2|l_3m_3\rangle$ represents the so-called Gaunt coefficients ([60], pp. 751–754). Of course, in the case of a diatomic system lying on the **Z** axis the above relationship simplifies considerably since we have the relation $Y_l^m(k\pi,\varphi)=\sqrt{(2l+1)/(4\pi)}\delta_{m,0}$ in which k is an arbitrary integer. In the present investigation for which only overlap integrals are required, the BCLF occurring in the above equation is evaluated with the help of the **C**-matrix expansion developed in Sec. II C. More specifically, use of **C** matrices in this case is probably the best strategy since according to the above expression, overlaps are described by a finite expansion. However, when more complicated integrals are required (e.g., exchange integrals appearing when many-electron molecules are considered) use of the **T**-matrix expansion and its corresponding Lanczos-τ form allow one to overcome the numerical difficulties connected to the **C** matrices (cf. Sec. III).

The numerical values listed hereafter were obtained in the free-field case. This calculation was conducted with an atomic basis set in which the Slater exponents, i.e., ζ's, were kept identical for all AOs. Besides inducing useful simplifications in the analytical form of the overlaps, the major advantage of this constraint is to allow one to optimize this single nonlinear parameter in a very straightforward manner. Of course when using such a basis set the expansion of Eq. (26) will definitely require more AOs in order to achieve an acceptable accuracy (see Table III).

In a previous work, de Melo *et al.* [48] have used a linear combination of $1s$ and $2s$ STFs to study the electronic structure of H_2^+ experiencing a strong magnetic field. In spite of its small size, such an atomic basis set yielded a fairly good qualitative picture of the underlying physics appearing under such a regime. In the following, we will extend this work to include in the computational procedure as many STFs as we

TABLE IV. Ground-state binding energy of H_2^+ in a strong magnetic field.

Basis set[a]	ζ	E_1[b]	ζ	E_2[c]	ζ	E_3[d]	ζ	E_4[e]
1*s*	1.44	−1.880 467 0	1.96	−2.491 875 7	3.16	−2.757 095 2	8.98	17.436 005 2
2*s*, 2*p*	2.04	−1.942 821 4	2.93	−2.727 876 3	4.86	−3.876 050 0	6.58	11.323 796 4
3*s*, 3*p*	2.51	−1.947 102 3	2.24	−2.759 804 7	3.68	−4.059 357 4	10.52	−0.511 950 1
4*s*, 4*p*, 3*d*	2.01	−1.949 860 2	2.88	−2.785 245 2	3.16	−4.282 665 0	9.44	−7.412 754 4
5*s*, 5*p*, 4*d*	1.77	−1.949 941 2	2.58	−2.790 132 9	4.36	−4.327 881 9	13.04	−8.656 907 6
6*s*, 6*p*, 5*d*, 4*f*	2.07	−1.949 964 9	3.16	−2.790 541 9	5.34	−4.332 656 6	15.52	−8.965 714 3
E (Ref. [50])		−1.949 800 0		−2.790 300 0		−4.350 000 0		−10.270 000
E (Ref. [48])		−1.881 700 0		−2.513 700 0				

[a] An atomic basis set of the form $\{As,Bp,Cd,\ldots\}$ includes the AOs of the form $\{\{1s,2s,\ldots,As\},\{2p,3p,\ldots,Bp\},\{3d,4d,\ldots,Cd\},\ldots\}$.

[b–e] Energy values (in Ry) were obtained with the parameters $\beta=1$, $R=1.752$ a.u. for b, $\beta=3$, $R=1.376$ a.u. for c, ($\beta=10$, $R=0.958$ a.u.), and ($\beta=100$, $R=0.448$ a.u.).

please. The increasing size of the basis set will not only allow us to improve the accuracy of the values given in Ref. [48] but much more important to handle stronger magnetic fields. Indeed, the variational wave function constructed with spherical STFs is expected to converge reasonably well in the case where the electronic cloud is not sufficiently deformed, that is to say when the spherical symmetry of the Coulomb potential dominates. However, for larger values of **B**, the wave function should be made flexible by incorporating nonspherical STFs in order to properly describe the new cylindrical symmetry of the system.

According to the definition of the molecular Hamiltonian, it may be seen that in addition to the integrals given by Eq. (27) we are also required to compute the following:

$$\begin{aligned}\mathcal{J}_1'&=\langle\chi_{n_1,l_1,m_1}(\zeta_1\mathbf{R}_a)|\rho^2|\chi_{n_2,l_2,m_2}(\zeta_2\mathbf{R}_a)\rangle,\\ \mathcal{J}_2'&=\langle\chi_{n_1,l_1,m_1}(\zeta_1\mathbf{R}_a)|\rho^2|\chi_{n_2,l_2,m_2}(\zeta_2\mathbf{R}_b)\rangle.\end{aligned}\tag{29}$$

Fortunately from Fig. 1 it may be readily seen that ρ which is the distance from the electron to the **Z** axis may be expressed as follows:

$$\rho=R\ \sin\ \theta=R_a\sin\ \theta_a=R_b\sin\ \theta_b\,.\tag{30}$$

Consequently, use of the above relations in Eq. (30) helps one to express the original two- and three-center integrals (29) in terms of one- and two-center quantities. Accordingly, the integrals arising when a magnetic field is applied to a linear molecule lying on the **Z** axis may be evaluated using the same numerical procedures already developed in the field-free case. To illustrate this, we show in the following how integrals (29) relate to those of Eq. (27). For such a purpose let us consider the integral $\mathcal{J}_2'$, Eq. (29), in which ρ is replaced by $R_a\ \sin\ \theta_a$:

$$\begin{aligned}\mathcal{J}_2'&=\langle\chi_{n_1,l_1,m_1}(\zeta_1,\mathbf{R}_a)|R_a^2\sin^2(\theta_a)|\chi_{n_2,l_2,m_2}(\zeta_2,\mathbf{R}_b)\rangle\\ &=\tfrac{2}{3}\langle\chi_{n_1,l_1,m_1}(\zeta_1,\mathbf{R}_a)|R_a^2[1-\sqrt{5/(4\pi)}\mathcal{Y}_2^0(\mathbf{R}_a/R_a)]|\chi_{n_2,l_2,m_2}(\zeta_2,\mathbf{R}_b)\rangle.\end{aligned}\tag{31}$$

With the help of the multiplication theorem of surface spherical harmonics, the above relationship may be rewritten in such a way as to obtain an overlap integral-based formula:

$$\begin{aligned}\mathcal{J}_2'=\frac{2}{3(2\zeta_1)^2}\left[\frac{[2(n_1+2)]}{(2n_1)!}\right]^{1/2}\Bigg\{&S_{n_1+2,l_1,m_1}^{n_2,l_2,m_2}(\zeta_1,\zeta_2,\mathbf{b})\\ &-(-1)^{m_1}\sqrt{5/(4\pi)}\sum_{l=|l_1-2|}^{l_1+2}{}''\langle 20|l_1m_1|l-m_1\rangle\\ &\times S_{n_1+2,l,m_1}^{n_2,l_2,m_2}(\zeta_1,\zeta_2,\mathbf{b})\Bigg\}.\end{aligned}\tag{32}$$

As in the free-field case, we have listed in Table IV the values of the the binding energy of H_2^+ in its ground state for various combinations of AOs.

Perhaps the most important feature of these values is the poor convergence that appears for increasing values of the magnetic field. Indeed, for large values of **B**, i.e., $\geqslant 10$ a.u., the discrepancy between our results and the benchmarks of Kravchenko and Liberman [59] becomes more pronounced. Here, it should be noticed that in their calculations these authors used very large Gaussian basis sets which were constructed following the approach devised by Schmidt and Ruedenberg [61] allowing one to attain completeness at infinity.

In the case of a 100 a.u. **B** field, our value calculated with the largest basis set given in Table IV ($\zeta=20.69$) is −6.420 44 a.u. while the value of Kravchencko and Liberman is -7.1276 a.u. The poor convergence encountered in our calculation has essentially two different origins. On the one hand and as mentioned in the field-free case, a basis set involving only one exponent simplifies the mathematics and the optimization work but requires more basis functions to achieve an acceptable accuracy. On the other hand, examination of the electron density corresponding to several values of **B** (Fig. 2) shows that for increasing values of the magnetic field the ''almost'' spherical symmetry of $H_2{}^+$ (when $\mathbf{B}=\mathbf{0}$) [Fig. 2(a)] steadily disappears in favor of a more cylindrical shape [Fig. 2(c)]. As a consequence the LCAO-type expansion (26) in terms of STF (involving spherical harmonics) will ultimately require more and more terms as **B** increases.

V. CONCLUDING REMARKS

Throughout the present work, useful expansions of BCLFs were presented and applied to study the behavior of $H_2{}^+$ experiencing a strong magnetic field. In the first part, the basic ideas needed in deriving a computationally oriented **C**-matrix formulation of the addition theorem of STFs were highlighted. This method exploits the fact that solid spherical harmonics satisfy a very simple addition theorem which allows one to introduce a **C**-matrix-type expansion only for the spherical part involved in STFs. Accordingly, it was shown that not only these matrices are symmetrical but much more important they can be generated recursively starting with **C** matrices occurring in the addition theorem of the Yukawa potential. The second part is devoted to improve the series expansion previously proposed by one of us [43]. Our analytical study led us to define a new infinite matrix which has the advantage of having a unique definition regardless of the space region. In addition, the analytical form of the infinite series presented in this work allowed us to obtain its polynomial approximate through the so-called Lanczos-τ method. The application of our new **C**-matrix formulation was illustrated in the third part where we have addressed the study of the hydrogen molecular ion subjected to a strong magnetic field. This molecular system which in the field-free case may be considered as trivial leads to a complex situation when experiencing a strong magnetic field. Indeed, addition of external fields into the Hamiltonian yields complex equations especially when nuclei are assumed to have finite masses [62]. Furthermore, from the values listed in Table IV it clearly appears that for increasing values of **B** the expansion in terms of STFs suffers from a poor convergence which is essentially due to the difficulty of representing the electron density by spherical harmonics. Improvements of these results can be obtained by means of various strategies. First, one can increase the size of the basis set (with different exponents) making it approach completeness [59] but this, of course, has a practical limitation when polyatomic systems are considered. The second alternative is to incorporate in the form of the AOs the cylindrical peculiarity of the problem which normally would allow one to reduce the size of the basis set but on the other hand requires developing new methods to handle multicenter integrals.

ACKNOWLEDGMENTS

This work was financially supported by NSF Cooperative Agreement No. HDR-9707076, and by the U.S. Army High Performance Computing Research Center under the auspices of the Department of the U.S. Army, U.S. Army Research Laboratory Cooperative Agreement No. DAAH04-95-2-0003/Contract No. DAAH04-95-C-0008. A grant of computer time by the Florida State University (FSU) is gratefully acknowledged.

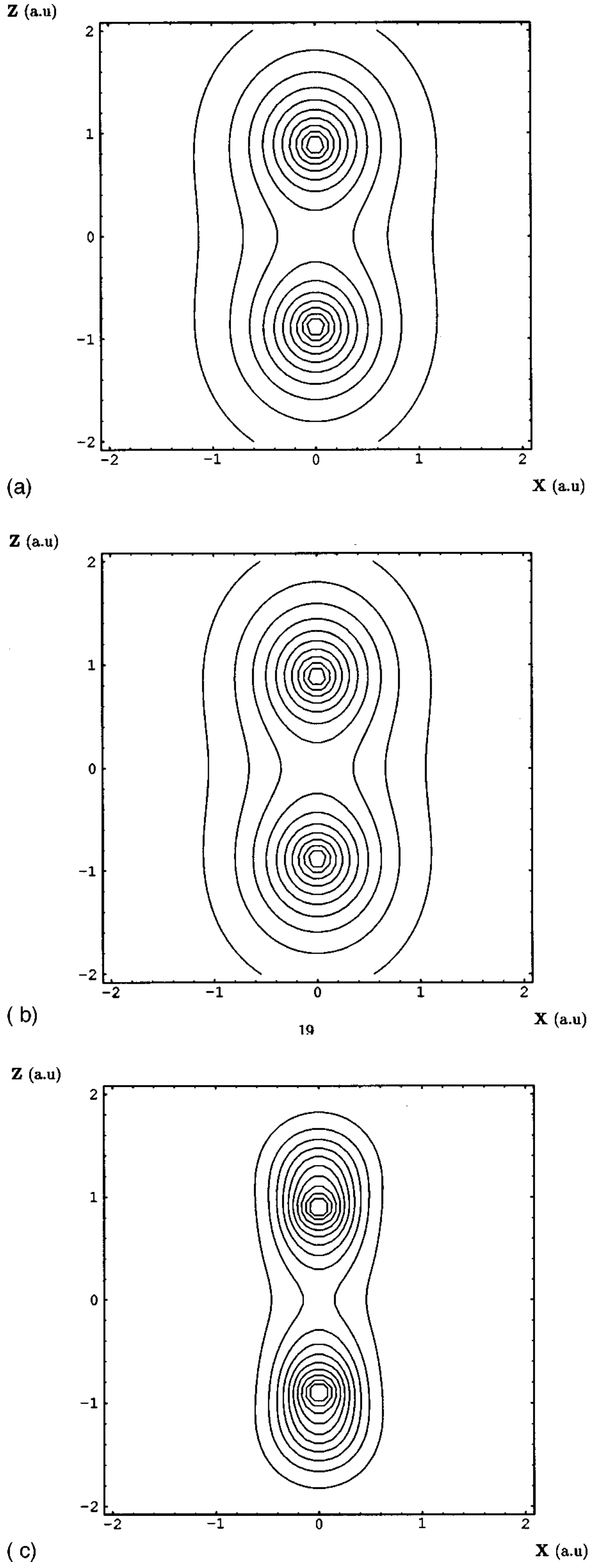

FIG. 2. Electron density contours calculated drawn for (a) $\beta=0$, (b) $\beta=1$ a.u., and (c) $\beta=10$ a.u. In all cases, the interatomic distance was kept constant.

APPENDIX: THE LANCZOS EXPANSION OF $_0F_1(;c;z)$

Throughout Sec. III we have discussed two different methods that can be used to calculate the coefficients involved in the polynomial approximation of BCLFs. In these procedures $\{a_{2q}^{(l)}\}_{0\leqslant q\leqslant N}$ are calculated numerically using a suitable recursive scheme. In the case under study, it is fortunately possible to derive the analytical formulas describing these coefficients. To do so, it should be noticed that the reduced Bessel function $\hat{\imath}_l(z)$ is closely related to the hypergeometric function $_0F_1(;l+3/2;z^2/4)$. Accordingly, the following discussion will be focused on the function $_0F_1(;c;z)$ which according to Ref. [37] satisfies the differential equation:

$$z^2\frac{d^2}{dz^2}W''(z)+c\frac{d}{dz}zW'(z)-zW(z)=0, \tag{A1}$$

where $W(z)$ stands for $_0F_1(;c;z)$. Now, if one assumes a polynomial approximation for the function $W(z)$, i.e., $W(z)=\Sigma_{p=0}^N b_p z^p$, the left hand side of Eq. (A1) takes the form

$$(-b_0+cb_1)z+\sum_{p=2}^{N}[-b_{p-1}+p(c+p-1)b_p]z^p+b_N z^{N+1}. \tag{A2}$$

Correspondingly, the perturbation term that will appear in the right hand side of Eq. (A1) will be a polynomial of degree $N+1$. In Lanczos's original method such a polynomial will be written as $\tau T_N^*(z/r_{\max})+\tau' T_{N+1}^*(z/r_{\max})$. Here, $T_n^*(z)$ represents the shifted Tchebyshev polynomial of degree n which according to Ref. [37] (pp. 210–212) may be written as

$$T_n^*(z)=\sum_{k=0}^{n}c_k^n z^k, \quad \text{with} \quad c_k^n=(-1)^{n+k}\left(\frac{4}{A}\right)^k\frac{n}{n+k}\binom{n+k}{2k}. \tag{A3}$$

As in Sec. III, equating expression (A2) with Eq. (A3) will give a linear system similar to that given by Eq. (21). In addition, the first of these equations yields $\tau=-\tau'$. Hence, taking the latter equality into account one can write

$$\begin{pmatrix} -1 & c & 0 & 0 & \cdots & 0 & 0 & \cdots & 0 \\ 0 & -1 & 2(c+1) & 0 & \cdots & 0 & 0 & \cdots & 0 \\ 0 & 0 & -1 & 3(c+2) & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & 0 \\ 0 & 0 & 0 & 0 & \cdots & -1 & (p+1)(c+p) & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 & 0 & \cdots & -1 \end{pmatrix} \begin{pmatrix} b_0' \\ b_1' \\ b_2' \\ \vdots \\ b_p' \\ \vdots \\ b_n' \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_p \\ \vdots \\ C_{n+1} \end{pmatrix}, \tag{A4}$$

where C_k stands for the kth coefficient appearing in the polynomial $T_{n+1}^*(z)-T_n^*(z)$. In addition, for practical reasons we prefer to introduce the new variable b_p' such that $b_p'=b_p/\tau'$. To solve the above linear system, it is advisable to use the well-known Cramer rule. In the case under study it may easily be shown that the determinant of the above system is defined by $\Delta=(-1)^{n+1}$. As regards, the determinant corresponding to the pth unknown, that is, b_p', it may be written as

$$\Delta_{b_p'}=\begin{vmatrix} -1 & c & 0 & \cdots & C_1 & \cdots & 0 \\ 0 & -1 & 2(c+1) & \cdots & C_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \ddots & 0 \\ 0 & 0 & 0 & \cdots & C_p & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & C_{n+1} & \cdots & -1 \end{vmatrix}. \tag{A5}$$

The expansion of this determinant with respect to the column of the constants C_p yields after some algebraic manipulations the following expression:

$$\begin{aligned}\Delta_{b_p'}&=(-1)^n\sum_{k=p}^{n}\left[\prod_{j=p}^{k-1}(j+1)(c+j)\right]C_{k+1}\\ &=(-1)^n\sum_{k=p}^{n}\frac{k!}{p!}\frac{(c)_k}{(c)_p}C_{k+1}.\end{aligned} \tag{A6}$$

Now, using the initial condition $_0F_1(;c;0)=b_0=1$ yields the definition of the parameter $\tau'=1/b_0'$. Furthermore, inserting the expression of τ' into that of b_p' allows us to finally derive the full analytical Lanczos-type expansion of $_0F_1(;c;z)$ in which the coefficients may be made explicit as

$$b_p=\tau b_p'=\frac{b_p'}{b_0'}=\frac{\sum_{k=p}^{n}(k!/p!)[(c)_k/(c)_p]C_{k+1}}{\sum_{k=0}^{n}k!(c)_k C_{k+1}}. \tag{A7}$$

From the above expression, it may readily be seen that the coefficients b_p and b_{p+1} are connected by the following recurrence relation:

$$b_{p+1}=\frac{1}{(p+1)(c+p)}\left[b_p-\frac{C_{p+1}}{\sum_{k=0}^{n} k!(c)_k C_{k+1}}\right] \quad \text{with } b_0=1. \tag{A8}$$

Here, it should be noticed that the first term appearing in the above equation defines the exact recurrence relation defining the coefficients of the series representation of ${}_0F_1(;c;z)$. The second term is a correction to such coefficients resulting from the polynomial (i.e., truncation) approximation.

However, for computational purposes it is more advantageous to first evaluate by means of a backward recursive relation the partial sums

$$s_n=\frac{(-1)^n}{2}\left(\frac{4}{A}\right)^n \frac{n!}{(a)_{n+1}},$$
$$s_p=\sum_{k=p}^{n} k!\,\frac{(c)_k}{(c)_n}\,\frac{c_k^n}{(a)_{k+1}}, \quad \text{with } p=n-1,n-2,\ldots,0. \tag{A9}$$

From this point, obtaining the coefficients b_p is of course straightforward. Before going further, it is of importance to underline that, in our case, although the Lanczos-τ method allows us to obtain a useful polynomial approximation of the Kummer function, the evaluation of such a polynomial may, however, suffer from severe numerical instabilities. Indeed, from Eq. (A7), it may be seen that the polynomial coefficients b_p have alternating signs which in other words means that loss of significant digits is to be expected if the negative and the positive part are nearly equal. Such a troublesome situation may be avoided if one uses quadruple precision and expresses the Lanczos polynomial as a difference of two terms since the coefficients b_p may be written such that

$$b_p=(-1)^p\,\frac{(a)_p}{p!(c)_p}-(-1)^p\,\frac{(a)_p}{p!(c)_p} \times\frac{\sum_{k=0}^{p-1}(-1)^k k![(c)_k/(a)_{k+1}]c_k^n}{\sum_{k=0}^{n}(-1)^k k![(c)_k/(a)_{k+1}]c_k^n}. \tag{A10}$$

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