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Prolate-spheroidal orbitals for homonuclear and heteronuclear diatomic molecules. I. Basic procedure

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In view of further determination of shielded homonuclear and heteronuclear diatomic orbitals, the problem of one electron in the field of two fixed nuclei and a cylindrically symmetric parametric potential is investigated. The simultaneous resolution of the separated equations, in prolate-spheroidal coordinates, is performed by a matricial technique using a Newton-Raphson scheme; as the orbitals are expanded in terms of orthogonal functions only symmetric band matrices are involved. Calculation of monoelectronic and bielectronic integrals is described.

I. INTRODUCTION

The solutions of the problem of one electron moving in the field of two fixed nuclei should occupy much the same position in approximate treatments of diatomics, and even to some extent of polyatomic molecules, as the general hydrogenic functions occupy in the treatment of complex atoms. Nevertheless, the use of these functions, i.e., diatomic orbitals (DO), within the one-configuration molecular-orbital scheme has not been very successful,[1,2] owing to the difficulty of taking into account the interelectronic interactions and, moreover, owing to the complexity of calculations. For one-electron diatomic systems, although various forms of the DO solutions have been obtained with great numerical accuracy,[3-20] the many-electron case has not been extensively studied.[1,2,17,21]

In atomic problems, considerable success has been achieved by using an "effective nuclear charge" to represent, in an average way, the electronic correlation. Within the diatomic-spheroidal-orbital (DO) scheme, the systematic introduction of screening effects (or of an effective potential that may be considered as a first step toward the construction of a separable Hartree-Fock-like solution) can be attempted following the general features which have been described by Teller and Sahlin.[17] The application of these methods calls for the resolution of equations analogous to those of the single-electron case; it is then necessary to have at hand a reliable and accurate method of resolution to treat either homonuclear or heteronuclear diatomics, for any values of the charges Z_A, Z_B and of the internuclear distance R on which the diatomic shielding effects depend.

In the present paper, the systematic determination of both homonuclear and heteronuclear DO orbitals by a matricial technique within a direct Newton-Raphson scheme is reinvestigated. Our procedure differs, in some points, from other previous works[1-21]; i.e., it introduces a different expansion of the functions in order to always deal with symmetric-band matrices. The main purpose of this paper is to give the theoretical background necessary when considering the shielding problem and further use of DO orbitals in molecular calculations. It is not our intention to present extensive tables of DO orbitals for various values of R, and only few illustrative and comparative test results will be given.

II. THEORY

Within the Born-Oppenheimer approximation, the Schrödinger equation for the one-electron two-center problem, with the charges Z_A, Z_B at the distance R (as foci), is

$$\left[\Delta + 2\left(\frac{Z_A}{r_A} + \frac{Z_B}{r_B}\right) + 2E\right]\psi = 0. \tag{1}$$

It is well known that Eq. (1) is separable when introducing prolate spheroidal coordinates.

A. Separation of the Schrödinger equation

Let us define prolate-spheroidal coordinates (Fig. 1):

$$\lambda = (r_A + r_B)/R, \quad 1 \leq \lambda < \infty$$

$$\mu = (r_A - r_B)/R, \quad -1 \leq \mu \leq 1$$

$$0 \leq \varphi \leq 2\pi.$$

The electronic bound-state wave function can then be factorized and written

$$\psi(\lambda, \mu, \varphi) = \Lambda(\lambda) M(\mu, \varphi) = \Lambda(\lambda) G(\mu) e^{\pm i m \varphi}.$$

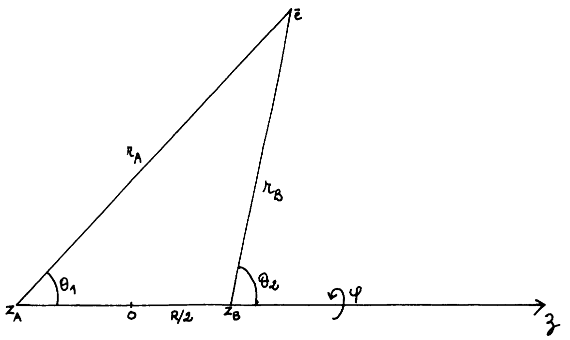

FIG. 1. Prolate spheroidal coordinates.

The functions $\Lambda(\lambda)$ and $M(\mu, \varphi)$ are, respectively, solutions of the following pair of differential equations[3,7]:

$$\left[\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)-\frac{m^2}{1-\mu^2}+p^2\mu^2-R(Z_A-Z_B)\mu-A\right]\times M(\mu,\varphi)=0, \tag{2}$$

$$\left[\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right)-\frac{m^2}{\lambda^2-1}-p^2\lambda^2+R(Z_A+Z_B)\lambda+A\right]\times\Lambda(\lambda)=0, \tag{3}$$

where p is the energy parameter, i.e., $E=-2p^2/R^2$ (a.u.).

A is the characteristic value of the invariant operator[18,22]

$$\mathcal{A}=-L^2-\frac{R^2}{4}\left(\Delta-\frac{\partial^2}{\partial z^2}\right)-R(Z_A\cos\theta_1-Z_B\cos\theta_2)-p^2. \tag{4}$$

$\vec{L}$ is the orbital angular momentum of the electron. At the limit $R=0$, since $p^2=0$ as well, $\mathcal{A}$ reduces to $-L^2$ and the corresponding eigenvalue is therefore $A=-l(l+1)$. Hereafter, the united atom labeling (n, l) of the states will be used.

B. Wave functions

In order to transform the resolution of the coupled differential equations (2) and (3) into the determination of the simultaneous eigenvalues of a pair of symmetric band matrices, we have assumed for the $M(\mu,\varphi)$ and $\Lambda(\lambda)$ solutions an expansion in terms of orthonormal functions.

(i) For both homonuclear and heteronuclear cases, the function $M(\mu,\varphi)$ is expanded as a linear combination of spherical harmonics, i.e.,

$$M(\mu,\varphi)=\sum_{k=m}^{\infty} f_k^m Y_k^m(\mu,\varphi). \tag{5}$$

For the heteronuclear case $(Z_A \neq Z_B)$, all the consecutive values of k are to be considered. For the homonuclear case $(Z_A=Z_B)$, since Eq. (2) becomes even in the μ variable, the function $M(\mu,\varphi)$ is even in μ; consequently the integer k in the expansion (5) must keep the same parity, i.e., the values of k jump by steps of two units.

When truncating the expression (5) $(k=m, K)$, the resolution of Eq. (2) becomes equivalent to the resolution of the following matrix equation:

$$[\mathcal{F}(p,A)]\,|f|=0. \tag{6}$$

$[\mathcal{F}(p,A)]$ is a symmetric $(K-m+1)$-dimensional band matrix and $|f|$ is a $(K-m+1)$-dimensional vector, the components of which are the f_k^m coefficients $(k=m, K)$.

When using some of the functional relationships between spherical harmonics and making explicit the Wigner $3j$ symbols, we obtain the following expressions of the nonvanishing matrix elements of $[\mathcal{F}(p,A)]$ [23]:

$$F_{i,i}(p,A)=-i(i+1)+p^2\left(\frac{2i^2-2m^2+2i-1}{(2i+3)(2i-1)}\right)-A,$$

$$F_{i,i+1}(p,A)=F_{i+1,i}(p,A)=-R(Z_A-Z_B)\left(\frac{(i+m+1)(i-m+1)}{(2i+1)(2i+3)}\right)^{1/2},$$

$$F_{i,i+2}(p,A)=F_{i+2,i}(p,A)=\frac{p^2}{(2i+3)}\left(\frac{(i+m+1)(i-m+1)(i+m+2)(i-m+2)}{(2i+1)(2i+5)}\right)^{1/2}. \tag{7}$$

For the heteronuclear case the matrix $[\mathcal{F}(p,A)]$ is a pentadiagonal matrix. Obviously, for the homonuclear case $(Z_A=Z_B)$, the off-diagonal matrix elements $F_{i+1,i}(p,A)$ vanish [Eq. (7)] owing to the particular structure of the vector $|f|$ (k jumping by steps of two units); by an appropriate relabeling of its elements, the matrix $[\mathcal{F}(p,A)]$ can be telescoped to an effective tridiagonal matrix acting on a corresponding telescoped vector.

(ii) Alternatively, for the $\Lambda(\lambda)$ function, in order to always deal with symmetric matrices, we choose an Hylleraas-like expansion[5]:

$$\Lambda(\lambda)=e^{-p(\lambda-1)}[2p(\lambda-1)]^{m/2}\times\sum_{n=m/2}^{\infty}C_{n-(m/2)}\mathcal{L}_{n-(m/2)}^{m}[2p(\lambda-1)], \tag{8}$$

where $\mathcal{L}_i^j(x)$ is the normalized associated Laguerre polynomial[24]

$$\mathcal{L}_i^j(x)=\left(\frac{i!}{(i+j)!}\right)^{1/2}L_i^j(x),$$

and

$$L_i^j(x)=\sum_{l=0}^{i}(-1)^l\binom{i+j}{i-l}\frac{x^l}{l!}. \tag{9}$$

Moreover, when truncating the expansion (8) $[n-(m/2)=0,N]$, one is led to solve the following matrix equation[23]:

$$[\mathcal{Y}(p,A)]\,|C|=0, \tag{10}$$

with

$$[\mathcal{Y}(p,A)]=[\mathcal{R}(p,A)]+pm^2[\mathcal{B}(p)]^{-1}. \tag{11}$$

$[\mathcal{R}(p,A)]$ and $[\mathcal{B}(p)]$ are symmetric $(N+1)$-dimensional tridiagonal matrices and $|C|$ is a $(N+1)$-dimensional vector, the components of which are the $C_{n-(m/2)}$ coefficients $[n-\frac{1}{2}m=0,N]$.

Using some of the functional relationships between normalized associated Laguerre polynomials and their derivatives, we obtain the following expressions[23] for the nonvanishing matrix elements of $[\mathcal{B}(p)]$:

$$\begin{aligned}&b_{i,i}(p)=4p+2i+1,\\&b_{i,i+1}(p)=b_{i+1,i}(p)=-[(i-\tfrac{1}{2}m+1)(i+\tfrac{1}{2}m+1)]^{1/2},\end{aligned} \tag{12}$$

with $\det[\mathcal{B}(p)]\neq 0$.

The nonvanishing matrix elements of $[\mathcal{R}(p,A)]$ are given by

$$\begin{aligned}r_{i,i}(p,A)&=(2i+1)\left(\frac{R(Z_A+Z_B)}{2p}-i-1-2p\right)\\&\quad+\frac{m^2}{4}+i+R(Z_A+Z_B)-p^2+A,\\r_{i,i+1}(p,A)&=r_{i+1,i}(p,A)\\&=-[(i-\tfrac{1}{2}m+1)(i+\tfrac{1}{2}m+1)]^{1/2}\\&\quad\times\left(\frac{R(Z_A+Z_B)}{2p}-i-1\right).\end{aligned} \tag{13}$$

In order to obtain square-summable wave functions for each fixed value of the nuclear separation distance R, one must find solutions of Eqs. (6) and (10) corresponding to the same value of p and of A. This will be reached by an iterative procedure described in Sec. III and Appendixes A–C.

In view of our further studies of the many-electrons case and of the screening effects, it is necessary to consider both the calculation of the electronic integrals (see Appendix D) and the one-electron problem with an additional potential.

C. Introduction of a particular additional potential

Let us assume that this additional potential is

$$V(\lambda,\mu)=\{4/[R^2(\lambda^2-\mu^2)]\}[f(\lambda)+g(\mu)], \tag{14}$$

where $f(\lambda)$ is linear in λ and $g(\mu)$ is quadratic in μ, i.e.,

$$\begin{aligned}&f(\lambda)=R(a_0+a_1\lambda),\\&g(\mu)=R(b_0+b_1\mu+b_2\mu^2).\end{aligned} \tag{15}$$

When introducing this additional potential, the Schrödinger equation remains separable in μ and λ and the functions $M(\mu,\varphi)$ and $\Lambda(\lambda)$ are now solutions of the following pair of differential equations:

$$\left[\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right)-\frac{m^2}{1-\mu^2}+(p^2-Rb_2)\mu^2-R(Z_A-Z_B+b_1)\mu-(A+Rb_0)\right]M(\mu,\varphi)=0, \tag{16}$$

$$\left[\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right)-\frac{m^2}{\lambda^2-1}-p^2\lambda^2+R(Z_A+Z_B-a_1)\lambda+(A-Ra_0)\right]\Lambda(\lambda)=0. \tag{17}$$

As a consequence, the introduction of the additional potential [(14), (15)] results in a slight modification of the expressions (7) and (13) of the elements of the $[\mathcal{F}(p,A)]$ and $[\mathcal{R}(p,A)]$ matrices, which are now

$$\begin{aligned}&F_{i,i}(p,A)=-i(i+1)+(p^2-Rb_2)\left(\frac{2i^2-2m^2+2i-1}{(2i+3)(2i-1)}\right)-(A+Rb_0),\\&F_{i,i+1}(p,A)=F_{i+1,i}(p,A)=-R(Z_A-Z_B+b_1)\left(\frac{(i+m+1)(i-m+1)}{(2i+1)(2i+3)}\right)^{1/2},\\&F_{i,i+2}(p,A)=F_{i+2,i}(p,A)=\frac{p^2-Rb_2}{2i+3}\left(\frac{(i+m+1)(i-m+1)(i+m+2)(i-m+2)}{(2i+1)(2i+5)}\right)^{1/2},\end{aligned} \tag{18}$$

and

$$r_{i,i}(p,A)=(2i+1)\left(\frac{R(Z_A+Z_B-a_1)}{2p}-i-1-2p\right)+\tfrac{1}{4}m^2+i+R(Z_A+Z_B-a_1-a_0)-p^2+A,$$
$$r_{i,i+1}(p,A)=r_{i+1,i}(p,A)=-[(i-\tfrac{1}{2}m+1)(i+\tfrac{1}{2}m+1)]^{1/2}\left(\frac{R(Z_A+Z_B-a_1)}{2p}-i-1\right). \tag{19}$$

It should be noted that if the additional potential would contain $f(\lambda)$ and $g(\mu)$ polynomials of higher degree k, the same procedure would remain valid but the corresponding $[\mathcal{F}(p,A)]$ and $[\mathcal{R}(p,A)]$ matrices to be considered would become $(2k+1)$-diagonal band matrices.

III. SIMULTANEOUS RESOLUTION OF THE SEPARATED TWO-CENTER EQUATIONS

In order to find the pair of eigenvalues p and A, which classify the discrete quantum states and are to be common to both matrices (6) and (10), one can use a Newton-Raphson (NR) scheme. This method involves the computation of the numerical values of the determinants and their partial derivatives with respect to p and A. As the matrices $[\mathcal{F}(p,A)]$, $[\mathcal{R}(p,A)]$, and $[\mathcal{B}(p)]$ are band matrices, this calculation can be performed rather easily using recursion formulas. This is possible for tridiagonal matrices[16] (see Appendix A) and also for pentadiagonal matrices (see Appendix B).

Details of the NR method can be found elsewhere.[25] Briefly stated, the algorithm is as follows: starting from a pair of values p_i and A_i, one obtains improved values

$$p_{i+1}=p_i+\Delta p_i\,,\quad A_{i+1}=A_i+\Delta A_i$$

and iterates until convergence. Within the NR scheme

$$\Delta p_i=-\left[\{\det[\mathcal{F}(p,A)]\}_i\left(\frac{\partial}{\partial A}\det[\mathcal{Y}(p,A)]\right)_i-\{\det[\mathcal{Y}(p,A)]\}_i\left(\frac{\partial}{\partial A}\det[\mathcal{F}(p,A)]\right)_i\right]\Big/D(p_i,A_i), \tag{20}$$

$$\Delta A_i=\left[\{\det[\mathcal{F}(p,A)]\}_i\left(\frac{\partial}{\partial p}\det[\mathcal{Y}(p,A)]\right)_i-\{\det[\mathcal{Y}(p,A)]\}_i\left(\frac{\partial}{\partial p}\det[\mathcal{F}(p,A)]\right)_i\right]\Big/D(p_i,A_i), \tag{21}$$

where

$$D(p_i,A_i)=\left(\frac{\partial}{\partial A}\det[\mathcal{Y}(p,A)]\right)_i\left(\frac{\partial}{\partial p}\det[\mathcal{F}(p,A)]\right)_i-\left(\frac{\partial}{\partial p}\det[\mathcal{Y}(p,A)]\right)_i\left(\frac{\partial}{\partial A}\det[\mathcal{F}(p,A)]\right)_i. \tag{22}$$

One has to be careful when calculating the increments Δp_i and ΔA_i [see Eqs. (20) and (21)], because they are obtained as ratios of quantities the order of magnitude of which can vary on a large scale. In order to obtain the required accuracy, a suitable scaling factor is automatically adjusted by the computational routine.

Since good approximations for the starting values p_0 and A_0 are available, the use of the NR method seems adequate. For a given (n,l) state, where n and l are, respectively, the principal and the orbital quantum numbers within the hydrogenlike united-atom labeling, a good initial choice is

$$A_0=-l(l+1),\quad p_0=R(Z_A+Z_B)/2n.$$

Indeed, since A is the eigenvalue of the invariant operator $\mathcal{A}$ [see Eq. (4)], this choice of A_0 is valid particularly for small values of the internuclear distance R. Likewise, p_0 is a good approximation of p for small values of R, i.e., when the Bohr expression of the energy remains close to the true value. For large values of R, the initial values of A_0 and p_0 are extrapolated from the exact A and p corresponding to smaller R.

In general, the iterative process converges rapidly and the accuracy corresponds to $|A_{i+1}-A_i|<10^{-10}$. For a calculation of the determinants and their partial derivatives contained in the expressions (20) and (21) of Δp_i and ΔA_i, we take advantage of a separate consideration of the σ-type ($m=0$) and other types ($m\neq 0$) orbitals and also of a distinction between the homonuclear and the heteronuclear cases. Of course, for $m=0$, the matrix $[\mathcal{Y}(p,A)]$ [see Eq. (11)] reduces to the matrix $[\mathcal{R}(p,A)]$, i.e., to a tridiagonal symmetric matrix. Moreover, as was pointed out before, the matrix $[\mathcal{F}(p,A)]$[Eq. (7)], which is pentadiagonal for the heteronuclear case, reduces to a tridiagonal matrix for the homonuclear case.

A. Homonuclear case

(i) The matrix $[\mathcal{F}(p,A)]$ is tridiagonal for all states ($m=0$ and $m\neq 0$). The required values of its determinant and partial derivatives are calculated using the appropriate recursion formulas which are given in Appendix A.

(ii) The matrix $[\mathcal{Y}(p,A)]$ is tridiagonal for $m=0$, i.e., for σ-type orbitals, and the procedure described above is also used for calculating det$[\mathcal{Y}(p,A)]$ and its partial derivatives. For $m \neq 0$, i.e., non-σ-type orbitals, the calculation of det$[\mathcal{Y}(p,A)]$ and its partial derivatives needs a few more manipulations, which are given in Appendix C.

B. Heteronuclear case

(i) The matrix $[\mathcal{F}(p,A)]$ is now pentadiagonal for all states ($m=0$ and $m \neq 0$) and the required value of its determinant and partial derivatives are obtained by the recursion formulas of Appendix B.

(ii) The calculation scheme of det$[\mathcal{Y}(p,A)]$ and its partial derivatives is the same as in the homonuclear case.

Our procedure is straightforward and differs, for the heteronuclear case, from the Helfrich method.[20] Indeed, to eliminate the manipulations of pentadiagonal matrices, he has to introduce an exponential term $e^{\pm p\mu}$ that enables him to keep the tridiagonal structure of the corresponding matrix. On the other hand, however, he has to operate in two stages: first he determines the characteristic values p and A by the NR scheme for the tridiagonal matrix; then, using these values p and A, he finds the $|f|$ vector by diagonalizing the pentadiagonal matrix $[\mathcal{F}(p,A)]$.

IV. SOME ILLUSTRATIVE RESULTS

Using the outlined matricial procedure coupled with the Newton-Raphson scheme, a computer program has been written (double precision IBM 360-75) which, for any value of m and of the internuclear distance R, gives the values of the total energy E_T, of the separation constant A, and of the coefficients f_i^m and C_i characterizing the diatomic orbital. This program eventually takes into account the additional potential, Eqs. (14) and (15). Various calculations have been carried out in order to experiment with the effective truncation of the expansions (5) and (8) of the eigenfunctions $M(\mu,\varphi)$ and $\Lambda(\lambda)$; we found that, in general, for a 10^{-8} accuracy of the p and A values, a sufficient value of the number of basis functions is $K=10$ for the $M(\mu,\varphi)$ function and $N=10$ for the $\Lambda(\lambda)$ function.

Illustrative results are given for H_2^+ and some heteronuclear ions (HeH^{++}, LiH^{3+}, and $LiHe^{4+}$) and checked with other previous results, when available elsewhere.[7-21] The expansion coefficients of the $1s\sigma$ diatomic orbital ($R=2$ a.u.) as well as the values of the total energy E_T, of p and of the separation constant A are collected in Table I. In Table II are gathered results concerning some other diatomic orbitals at the equilibrium distance.

In both tables, coefficients less than 10^{-6} that have no significant influence on the total energy value are not given. From experience we found that, when R increases, the λ expansion (8) of the eigenfunction $\Lambda(\lambda)$ converges rapidly, i.e., the number of significant coefficients decreases, whereas one observes the reverse situation for the expansion (5) of $M(\mu,\varphi)$. However, this last

TABLE I. Parameters (in a.u.) and coefficients of the $1s\sigma$ diatomic orbital ($R=2$ a.u.).

		H_2^+	HeH^{2+}	LiH^{3+}	$LiHe^{4+}$
A		0.811 729 58	3.157 838 03	8.060 296 00	7.133 389 40
p		1.485 014 62	2.241 514 23	3.162 923 34	3.319 449 77
Total energy E_T		−0.602 634 21	−1.512 193 02	−3.502 042 02	−2.509 373 39
$M(\mu,\varphi)$ Coefficients	f_0	0.993 269	0.748 159	0.587 716	0.608 209
	f_1		0.593 131	0.665 538	0.651 372
	f_2	0.115 781	0.283 490	0.415 845	0.411 716
	f_3		0.087 039	0.184 912	0.178 601
	f_4	0.003 314	0.022 175	0.064 554	0.063 564
	f_5		0.004 374	0.018 465	0.018 032
	f_6	0.000 044	0.000 765	0.004 491	0.004 500
	f_7		0.000 111	0.000 947	0.000 951
	f_8		0.000 015	0.000 176	0.000 183
	f_9		0.000 002	0.000 029	0.000 031
$\Lambda(\lambda)$ Coefficients	C_0	0.998 825	0.999 451	0.999 822	0.999 369
	C_1	−0.048 330	−0.033 067	−0.018 821	−0.035 498
	C_2	−0.003 562	−0.001 824	−0.000 872	−0.001 089
	C_3	−0.000 562	−0.000 222	−0.000 086	−0.000 091
	C_4	−0.000 123	−0.000 038	−0.000 012	−0.000 012
	C_5	−0.000 029	−0.000 008	−0.000 002	−0.000 002
	C_6		−0.000 002		

TABLE II. Parameters (in a.u.) and coefficients of some diatomic orbitals at the equilibrium distance.

		$H_2{}^+$	HeH^{2+}	LiH^{3+}
Orbital		$2p\pi_u$	$2p\sigma$	$3d\sigma$
R		8.0	4.0	6.0
A		0.053 717 32	0.799 708 68	0.725 385 67
p		2.881 725 21	2.872 046 39	4.267 630 24
Total energy E_T		−0.134 510 63	−0.531 081 31	−0.511 814 88
$M(\mu,\varphi)$ Coefficients	f_0		0.735 448	0.571 320
	f_1		−0.655 959	−0.720 374
	f_2	0.976 251	0.032 882	0.356 706
	f_3		−0.164 996	−0.054 514
	f_4	0.216 001	−0.017 807	0.148 141
	f_5		−0.014 463	0.039 650
	f_6	0.016 621	−0.001 746	0.029 204
	f_7		−0.000 640	0.007 945
	f_8	0.000 653	−0.000 072	0.002 928
	f_9		−0.000 017	0.000 675
$\Lambda(\lambda)$ Coefficients	C_0	0.989 758	0.995 477	0.993 201
	C_1	−0.142 714	−0.094 997	−0.115 486
	C_2	0.003 356	0.000 637	0.005 343
	C_3	0.000 174	0.000 038	0.000 052
	C_4	0.000 019	0.000 004	0.000 003
	C_5	0.000 003		

point is not significantly complicated since, when calculating the matrix elements, the μ part is integrated analytically using Wigner $3j$ symbols. From the comparison of our results to those of Bates and Carson[10] for the HeH^{++} ($R=2$ and $R=5$ a.u.) DO $1s\sigma$, it appears that the introduction of the exponential factor $e^{\pm p\mu}$ in the μ expansion (5) of $M(\mu,\varphi)$ does not improve the convergence.

As a matter of curiosity, using our program for $Z_B=Z$ and $Z_A=0$ (or $Z_A=Z$ and $Z_B=0$), we obtained the diatomic orbitals of the hydrogenic atoms. It should be noted that these orbitals are not eigenfunctions of L^2 but of the $\mathcal{A}$ operator [see Eq. (4)]. As expected, we found that the μ expansion does not reduce to one term. Of course, we found again the $-Z^2/2n^2$ value of the energy.

From the few available previous results[1,2] and our preliminary calculations with DO's, for the two-electron molecules, we concluded, as expected, that it is necessary to include screening effects by considering shielded diatomic (SDO) orbitals. The determination of these SDO orbitals as well as their connection with a separable Hartree-Fock scheme[17] is investigated in a following paper that largely makes use of the results of the present paper.

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APPENDIX A: CALCULATION OF THE DETERMINANT OF A TRIDIAGONAL MATRIX AND PARTIAL DERIVATIVES

Let us consider an n-dimensional tridiagonal matrix $[\mathfrak{M}_n]$, i.e., one whose only nonvanishing current matrix elements are those labeled $m_{i,j}$ with $|i-j|\leq 1$. The value of the determinant $\det[\mathfrak{M}_n]$ and its partial derivatives is easily calculated by use of the following two-terms recursion formula:

$$\det[\mathfrak{M}_k]=m_{k,k}\det[\mathfrak{M}_{k-1}]-m_{k-1,k}\,m_{k,k-1}\det[\mathfrak{M}_{k-2}], \tag{A1}$$

where k runs from 2 to n and the initial values are

$$\begin{aligned}&\det[\mathfrak{M}_0]=1,\\&\det[\mathfrak{M}_1]=m_{1,1}.\end{aligned} \tag{A2}$$

When taking the partial derivatives of the expressions (A1) and (A2) with respect to a variable x, one gets

$$\frac{\partial}{\partial x}\det[\mathfrak{M}_k]=\det[\mathfrak{M}_{k-1}]\frac{\partial}{\partial x}(m_{k,k})+m_{k,k}\frac{\partial}{\partial x}\det[\mathfrak{M}_{k-1}]-\det[\mathfrak{M}_{k-2}]$$
$$\times\left(m_{k,k-1}\frac{\partial}{\partial x}(m_{k-1,k})+m_{k-1,k}\frac{\partial}{\partial x}(m_{k,k-1})\right)-m_{k-1,k}m_{k,k-1}\frac{\partial}{\partial x}\det[\mathfrak{M}_{k-2}] \tag{A3}$$

and

$$\frac{\partial}{\partial x}\det[\mathfrak{M}_0]=0,$$
$$\frac{\partial}{\partial x}\det[\mathfrak{M}_1]=\frac{\partial}{\partial x}(m_{1,1}). \tag{A4}$$

APPENDIX B: CALCULATION OF THE DETERMINANTS AND PARTIAL DERIVATIVES OF A PENTADIAGONAL MATRIX

Let us consider an n-dimensional pentadiagonal matrix $[\mathfrak{M}_n]$, i.e., one whose only nonvanishing current matrix elements are those labeled $m_{i,j}$ with $|i-j|\leq 2$. From each current k-dimensional matrix $[\mathfrak{M}_k]$, let us define the two $(k-1)$-dimensional associated matrices: $[\mathfrak{M}'_{k-1}]$ is formally obtained from $[\mathfrak{M}_k]$ by suppressing the kth column together with the $(k-1)$th row; $[\mathfrak{M}''_{k-1}]$ is formally obtained from $[\mathfrak{M}_k]$ by suppressing the kth column together with $(k-2)$th row. Hence, when expanding the three corresponding determinants with respect to the last column, one obtains

$$\det[\mathfrak{M}_k]=m_{k,k}\det[\mathfrak{M}_{k-1}]-m_{k-1,k}\det[\mathfrak{M}'_{k-1}]+m_{k-2,k}\det[\mathfrak{M}''_{k-1}], \tag{B1}$$

$$\det[\mathfrak{M}'_k]=m_{k-2,k}m_{k+1,k-1}\det[\mathfrak{M}'_{k-2}]-m_{k-1,k}m_{k+1,k-1}\det[\mathfrak{M}_{k-2}]+m_{k+1,k}\det[\mathfrak{M}_{k-1}], \tag{B2}$$

and

$$\det[\mathfrak{M}''_k]=m_{k-2,k}m_{k+1,k-1}m_{k,k-2}\det[\mathfrak{M}_{k-3}]-m_{k,k}m_{k+1,k-1}\det[\mathfrak{M}_{k-2}]+m_{k+1,k}\det[\mathfrak{M}'_{k-1}]. \tag{B3}$$

When substituting the expression (B3) of $\det[\mathfrak{M}''_k]$ in (B1), one gets the following couple of recursion formulas allowing the calculation of $\det[\mathfrak{M}_k]$ and of $\det[\mathfrak{M}'_k]$:

$$\begin{aligned}\det[\mathfrak{M}_k]={}&m_{k-2,k}m_{k-3,k-1}m_{k,k-2}m_{k-1,k-3}\det[\mathfrak{M}_{k-4}]\\&-m_{k-2,k}m_{k-1,k-1}m_{k,k-2}\det[\mathfrak{M}_{k-3}]\\&+m_{k,k}\det[\mathfrak{M}_{k-1}]-m_{k-1,k}\det[\mathfrak{M}'_{k-1}]\\&+m_{k-2,k}m_{k,k-1}\det[\mathfrak{M}'_{k-2}],\end{aligned} \tag{B4}$$

$$\det[\mathfrak{M}'_k]=m_{k-2,k}m_{k+1,k-1}\det[\mathfrak{M}'_{k-2}]-m_{k-1,k}m_{k+1,k-1}\det[\mathfrak{M}_{k-2}]+m_{k+1,k}\det[\mathfrak{M}_{k-1}], \tag{B5}$$

where k runs from 2 to n and the initial values are

$$\det[\mathfrak{M}_0]=1,$$
$$\det[\mathfrak{M}_1]=m_{1,1}. \tag{B6}$$

The partial derivatives of $\det[\mathfrak{M}_k]$ are obtained by differentiating the expressions (B4)–(B6).

APPENDIX C: CALCULATION OF THE DETERMINANT OF THE MATRIX $[\mathcal{Y}(p,A)]$ FOR NON-σ-TYPE ORBITALS

When $m\neq 0$, the matrix $[\mathcal{Y}(p,A)]$ is no longer a band matrix, and from Eq. (11)

$$[\mathcal{Y}(p,A)]=[\mathcal{R}(p,A)]+pm^2[\mathcal{B}(p)]^{-1}. \tag{C1}$$

When right-multiplying both sides of (C1) by $[\mathcal{B}(p)]$, one gets

$$[\mathcal{T}(p,A)]=[\mathcal{Y}(p,A)][\mathcal{B}(p)]=[\mathcal{R}(p,A)][\mathcal{B}(p)]+pm^2. \tag{C2}$$

The matrix $[\mathcal{T}(p,A)]$, being the shifted product of the two-tridiagonal symmetrical matrices $[\mathcal{R}(p,A)]$ and $[\mathcal{B}(p)]$, is a nonsymmetrical pentadiagonal matrix, the nonvanishing elements of which are

$$\begin{aligned}t_{i,i\pm2}(p,A)&=r_{i,i\pm1}(p,A)b_{i\pm1,i\pm2}(p),\\t_{i,i\pm1}(p,A)&=r_{i,i}(p,A)b_{i,i\pm1}(p)\\&\quad+r_{i,i\pm1}(p,A)b_{i\pm1,i\pm1}(p),\\t_{i,i}(p,A)&=\sum_{l=i-1}^{i+1}r_{i,l}(p,A)b_{l,i}(p)+pm^2,\end{aligned} \tag{C3}$$

where the matrix elements $r_{i,j}(p,A)$ are given by Eq. (13) [or by (19) when the additional potential (14) is taken into account], and the matrix elements $b_{i,j}(p)$ are given by (12).

From the expression (C2)

$$\det[\mathcal{T}(p,A)]=\det[\mathcal{Y}(p,A)]\det[\mathcal{B}(p)],$$

and, since $\det[\mathcal{B}(p)]\neq 0$,

$$\det[\mathcal{Y}(p,A)]=\det[\mathcal{T}(p,A)]/\det[\mathcal{B}(p)].$$

Consequently,

$$\frac{\partial}{\partial A}\det[\mathcal{Y}(p,A)]=\left(\frac{\partial}{\partial A}\det[\mathcal{T}(p,A)]\right)\Big/\det[\mathcal{B}(p)]$$

and

$$\frac{\partial}{\partial p}\det[\mathcal{Y}(p,A)] = \left(\det[\mathcal{B}(p)]\,\frac{\partial}{\partial p}\det[\mathcal{T}(p,A)] - \det[\mathcal{T}(p,A)]\,\frac{\partial}{\partial p}\det[\mathcal{B}(p)]\right)\Big/(\det[\mathcal{B}(p)])^2 .$$

Since $[\mathcal{B}(p)]$ is a tridiagonal matrix, $\det[\mathcal{B}(p)]$ and $\{\partial(\det[\mathcal{B}(p)])/\partial p\}$ are easily calculated from formulas (A1) and (A3) of Appendix A; formulas (B4)–(B6) of Appendix B are used to calculate

$$\det[\mathcal{T}(p,A)],$$

$$\frac{\partial}{\partial A}\det[\mathcal{T}(p,A)],$$

and

$$\frac{\partial}{\partial p}\det[\mathcal{T}(p,A)].$$

APPENDIX D: CALCULATION OF THE ELECTRONIC INTEGRALS

A. The bielectronic repulsion integral J_{abcd}

$$J_{abcd} = \int\int \psi_a^*(\lambda_1,\mu_1,\varphi_1)\psi_b(\lambda_1,\mu_1,\varphi_1)\frac{1}{r_{12}} \times\psi_c(\lambda_2,\mu_2,\varphi_2)\psi_d^*(\lambda_2,\mu_2,\varphi_2)\,d\tau_1\,d\tau_2, \tag{D1}$$

where

$$\psi(\lambda,\mu,\varphi) = M(\mu,\varphi)\Lambda(\lambda).$$

The $M(\mu,\varphi)$ and $\Lambda(\lambda)$ functions are defined by Eqs. (5) and (8).

$$d\tau = \tfrac{1}{8}R^3(\lambda^2-\mu^2)\,d\lambda\,d\mu\,d\varphi.$$

One introduces the Neumann expression of $1/r_{12}$ in terms of the symmetrized associated Legendre functions of the first kind $\mathcal{P}_l^m(\lambda)$ and of the second kind $\hat{Q}_l^m(\lambda)$, and the spherical harmonics $Y_l^m(\mu,\varphi)$, i.e.,

$$\frac{1}{r_{12}} = \frac{8\pi}{R}\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\mathcal{P}_l^m(\lambda_1)\hat{Q}_l^m(\lambda_2)Y_l^m(\mu_1,\varphi_1)Y_l^{-m}(\mu_2,\varphi_2). \tag{D2}$$

Formula (D2) holds for $\lambda_1 < \lambda_2$; one has to exchange λ_1 and λ_2 in it for the case $\lambda_1 > \lambda_2$.

$$\mathcal{P}_l^m(\lambda) = \left(\frac{(l-m)!}{(l+m)!}\right)^{1/2} P_l^m(\lambda);$$

$$\hat{Q}_l^m(\lambda) = \left(\frac{(l-m)!}{(l+m)!}\right)^{1/2} Q_l^m(\lambda).$$

Then the integral J_{abcd} can be written

$$J_{abcd} = \frac{R^5}{32}\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\left(\int_1^{\infty}\hat{Q}_l^m(\lambda_1)\Lambda_a(\lambda_1)\Lambda_b(\lambda_1)\,d\lambda_1\int_1^{\lambda_1}\mathcal{P}_l^m(\lambda_2)\Lambda_c(\lambda_2)\Lambda_d(\lambda_2)\,d\lambda_2 + \int_1^{\infty}\hat{Q}_l^m(\lambda_2)\Lambda_c(\lambda_2)\Lambda_d(\lambda_2)\,d\lambda_2\int_1^{\lambda_1}\mathcal{P}_l^m(\lambda_1)\Lambda_a(\lambda_1)\Lambda_b(\lambda_1)\,d\lambda_1\right)J_{ab}(1,l)J_{cd}(2,l), \tag{D3}$$

where

$$J_{ab}(1,l) = \int_0^{2\pi}d\varphi_1\int_{-1}^{+1}Y_l^m(\mu_1,\varphi_1)\,M_a^*(\mu_1,\varphi_1)M_b(\mu_1,\varphi_1)(\lambda_1^2-\mu_1^2)\,d\mu_1$$

and its counterpart $J_{cd}(2,l)$ is defined by an analogous relationship ($1\to 2$, $a\to c$, $b\to d$). Since the $M(\mu,\varphi)$ functions are expanded in terms of spherical harmonics, the $J_{ab}(1,l)$ and $J_{cd}(2,l)$ are easily calculated, and one obtains

$$\begin{aligned} J_{ab}(1,l) &= \lambda_1^2A_{ab}(l) - B_{ab}(l),\\ J_{cd}(2,l) &= \lambda_2^2A_{cd}(l) - B_{cd}(l), \end{aligned} \tag{D4}$$

where

$$A_{ab}(l) = (2l+1)^{1/2}\sum_{k_a=m_a}^{K_a}\sum_{k_b=m_b}^{K_b}(-)^{m_a}f_{k_a}^{m_a}f_{k_b}^{m_b}[(2k_a+1)(2k_b+1)]^{1/2}\begin{pmatrix} l & k_a & k_b\\ m & -m_a & m_b\end{pmatrix}\begin{pmatrix} l & k_a & k_b\\ 0 & 0 & 0\end{pmatrix},$$

$$B_{ab}(l) = \frac{1}{3}A_{ab}(l) + (-)^{m_b}\frac{2}{3}(2l+1)^{1/2}\sum_{k_a=m_a}^{K_a}\sum_{k_b=m_b}^{K_b}f_{k_a}^{m_a}f_{k_b}^{m_b}\sum_{j=|l-2|,2}^{l+2}(2j+1)[(2k_a+1)(2k_b+1)]^{1/2} \times\begin{pmatrix} 2 & l & j\\ 0 & m & -m\end{pmatrix}\begin{pmatrix} 2 & l & j\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j & k_a & k_b\\ m & -m_a & m_b\end{pmatrix}\begin{pmatrix} j & k_a & k_b\\ 0 & 0 & 0\end{pmatrix}, \tag{D5}$$

and their counterparts $A_{cd}(l)$ and $B_{cd}(l)$ are defined by analogous relationships ($a \to c$, $b \to d$).

From the nonvanishing conditions of the Wigner $3j$ coefficients in (D5), one gets the following selection rules: $m = m_a - m_b = m_c - m_d$; l must have the same parity as $(k_a + k_b)$ as well as $(k_c + k_d)$.

The integration in μ can be carried out analytically, whereas one has to use a seminumerical method to integrate in λ.

When substituting in (D3) the expression (D4) of $J_{ab}(1, l)$ and $J_{cd}(2, l)$, one obtains

$$J_{abcd} = \frac{R^5}{16} \sum_l I_{abcd}(l),$$

where

$$I_{abcd}(l) = \int_1^\infty [\lambda_1^2 A_{ab}(l) - B_{ab}(l)] \hat{Q}_l^m(\lambda_1) \Lambda_a(\lambda_1) \Lambda_b(\lambda_1)\, d\lambda_1 \int_1^{\lambda_1} [\lambda_2^2 A_{cd}(l) - B_{cd}(l)] \mathcal{P}_l^m(\lambda_2) \Lambda_c(\lambda_2) \Lambda_d(\lambda_2)\, d\lambda_2 .$$

Using the Rüdenberg's transformation,[26] the integral $I_{abcd}(l)$ can be written

$$I_{abcd}(l) = \left[\frac{\hat{Q}_l^m(\lambda_1)}{\mathcal{P}_l^m(\lambda_1)} F_{ab}(l, \lambda_1) F_{cd}(l, \lambda_1) \right]_1^\infty + (-)^m \int_1^\infty \frac{1}{(\lambda_1^2 - 1)[\mathcal{P}_l^m(\lambda_1)]^2} F_{ab}(l, \lambda_1) F_{cd}(l, \lambda_1)\, d\lambda_1 ,$$

where

$$F_{ab}(l, \lambda_1) = \int_1^{\lambda_1} dz\, \mathcal{P}_l^m(z) [z^2 A_{ab}(l) - B_{ab}(l)]\, e^{-(p_a + p_b)(z-1)} [2p_a(z-1)]^{m_a/2} [2p_b(z-1)]^{m_b/2}$$
$$\times \sum_{n=m_a/2}^{N_a} \sum_{u=m_b/2}^{N_b} C_{n-m_a/2} C_{u-m_b/2} \mathcal{L}_{n-m_a/2}^{m_a}[2p_a(z-1)] \mathcal{L}_{u-m_b/2}^{m_b}[2p_b(z-1)] ,$$

and its counterpart $F_{cd}(l, \lambda_1)$ is defined by analogous relationships ($a \to c$, $b \to d$). At this stage we have used Wahl's[27] procedure to numerically terminate the remaining λ integrations; i.e., after a few manipulations we used a three-points Simpson rule for calculating the $F_{ij}(l, \lambda)$ and an N-points Simpson rule for calculating the $I_{abcd}(l)$.

B. Normalization of the DO orbitals

Since the DO orbitals are exact self-adjoint equations, they are orthogonal and we need only to calculate the normalization which can be performed analytically. Setting

$$\mathcal{S} = \frac{R^3}{8} \int_0^{2\pi} d\varphi \int_{-1}^{+1} d\mu \int_1^\infty (\lambda^2 - \mu^2)\, \psi_a^*(\lambda, \mu, \varphi) \psi_a(\lambda, \mu, \varphi)\, d\lambda ,$$

one obtains

$$\mathcal{S} = \frac{R^3}{8} \Bigg[\frac{1}{2p} \sum_{n=m}^{N} C_{n-m}^2 \Bigg(1 - B_{aa}(0) + \frac{2n+1}{p} + \frac{1}{4p^2} [(2n+1)^2 + (n-m)(n+m) + (n-m+1)(n+m+1)] \Bigg)$$
$$- \frac{1}{p^2} \sum_{n=m}^{N} C_{n-m} C_{n-m+1} \left(1 + \frac{n+1}{p} \right) [(n-m+1)(n+m+1)]^{1/2} + \frac{1}{4p^3} \sum_{n=m}^{N} C_{n-m} C_{n-m+2}$$
$$\times [(n-m+1)(n-m+2)(n+m+1)(n+m+2)]^{1/2} \Bigg] ,$$

with $m = \frac{1}{2} m_a$.

$B_{aa}(0)$ is a particular value of the expression (D5). The normalization constant of the $\psi(\lambda, \mu, \varphi)$ function is $\mathcal{S}^{-1/2}$.

C. Matrix elements $\mathcal{V}_{ab}$ of the additional potential $V(\lambda, \mu)$

$$\mathcal{V}_{ab} = \frac{R^3}{8} \int_0^{2\pi} d\varphi \int_{-1}^{+1} d\mu \int_1^\infty (\lambda^2 - \mu^2)\, \psi_a^*(\lambda, \mu, \varphi) V(\lambda, \mu) \psi_b(\lambda, \mu, \varphi)\, d\lambda ,$$

where

$$V(\lambda,\mu)=\frac{4}{R^2(\lambda^2-\mu^2)}\,(a_0+a_1\lambda+b_0+b_1\mu+b_2\mu^2).$$

Since the $M(\mu,\varphi)$ functions are expanded in terms of spherical harmonics, the integration in the μ and φ variables is easily performed in terms of $3j$ Wigner coefficients. For the integration in the λ variable, one has to distinguish between off-diagonal and diagonal matrix elements.

1. *Off-diagonal matrix elements*

$$\mathcal{V}_{ab}=\tfrac{1}{2}R\left([b_1D_{ab}+b_2B_{ab}(0)]\int_1^\infty \Lambda_a(\lambda)\Lambda_b(\lambda)\,d\lambda\right.$$
$$\left.+A_{ab}(0)\int_1^\infty [a_0+b_0+a_1\lambda]\Lambda_a(\lambda)\Lambda_b(\lambda)\,d\lambda\right),$$

where $A_{ab}(0)$ and $B_{ab}(0)$ are particular values of the expression (D5) and D_{ab} is defined as follows:

$$D_{ab}=(-)^{m_a}\sum_{k_a=m_a}^{K_a}\sum_{k_b=m_b}^{K_b} f_{k_a}^{m_a} f_{k_b}^{m_b}[(2k_a+1)(2k_b+1)]^{1/2}$$
$$\times\begin{pmatrix}1 & k_a & k_b\\ 0 & -m_a & m_b\end{pmatrix}\begin{pmatrix}1 & k_a & k_b\\ 0 & 0 & 0\end{pmatrix},$$

with $m_a=m_b$.

The integration in the λ variable are performed numerically by a Gaussian quadrature.

2. *Diagonal matrix elements*

The calculation of these elements is performed analytically and one obtains

$$\mathcal{V}_{aa}=\frac{R}{2}\left[\frac{1}{2p}\sum_{n=m}^{N} C_{n-m}^2\left(a_0+b_0+a_1+b_1D_{aa}+b_2B_{aa}(0)+\frac{2n+1}{2p}\,a_1\right)\right.$$
$$\left.-\frac{1}{2p^2}\sum_{n=m}^{N} C_{n-m}C_{n-m+1}\,a_1[(n-m+1)(n+m+1)]^{1/2}\right],$$

with $m=\tfrac{1}{2}m_a$.

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