

Prolate-spheroidal orbitals for homonuclear and heteronuclear diatomic molecules. II. Shielding effects for the two-electron problem

M. Aubert

Laboratoire de Chimie-Physique, Institut National des Sciences Appliquées de Lyon, 69621 Villeurbanne, France

N. Bessis and G. Bessis

Laboratoire de Spectroscopie et de Luminescence, Université Lyon I, 69621 Villeurbanne, France

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The determination of shielded diatomic orbitals (SDO) is investigated from the exact resolution, in prolate-spheroidal coordinates, of the two-center problem with an effective parametric potential. This potential, which is cylindrically symmetric in order to preserve the separability of the Schrödinger equation, is obtained either by classical electrostatic considerations or by a variational procedure. Calculations are carried out for two-electron diatomic systems, i.e., H_2 , He_2^{2+} , and HeH^+ in their ground state. From the results and also from theoretical considerations, these SDO appear to be close to self-consistent-field orbitals. Extension to the N -electron problem is considered.

I. INTRODUCTION

Recently, Teller and Sahlin¹ have sketched out a method for treating many-electron diatomic systems, within the diatomic-spheroidal-orbital scheme, without adding further difficulties to the treatment of one-electron diatomics. In order to partially take into account the interelectronic dynamic correlation, they introduce an effective potential that still preserves the separability of the one-electron two-center Schrödinger equation. Within the molecular-orbital scheme, this method is equivalent to building up the diatomic wave function from shielded diatomic orbitals (SDO) and can be considered, in some respects, as a pre-Hartree-Fock calculation. Up to now, to our knowledge, except for the H_2 molecule,¹⁻³ such SDO orbitals have not been determined.

In the present paper, the determination of SDO orbitals is investigated as exact solutions of a two-center problem with an effective parametric potential. The values of the parameters are found either by classical electrostatic considerations, or by a variational method. The basic procedure of determination of the SDO orbitals has been detailed in a previous paper⁴ (noted hereafter as I).

Calculations are carried out for two-electron diatomic systems, i.e., H_2 , He_2^{2+} , and HeH^+ in their ground state. Extension to N -electron systems and the determination of the corresponding successive SDO orbitals will be given in a forthcoming paper.

II. DETERMINATION OF AN EFFECTIVE POTENTIAL

The Schrödinger equation for the N -electron two-center problem with the charge Z_A, Z_B at distance R (as foci) is

$$\left[\sum_{i=1}^N \Delta_i + 2 \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) - 2 \sum_{i < j}^N \frac{1}{r_{ij}} + 2E \right] \psi = 0. \quad (1)$$

In order to keep the usual orbital picture of the many-electron problem and to reduce the solution of Eq. (1) to the simpler problem of solving one-particle equations, one has to introduce in an average way the interelectronic repulsion terms as a sum of one-particle effective potentials V_i .

A. Separated equations

When introducing prolate-spheroidal coordinates

$$\begin{aligned} \lambda &= (r_A + r_B)/R, & 1 \leq \lambda < \infty \\ \mu &= (r_A - r_B)/R, & -1 \leq \mu \leq +1 \\ 0 &\leq \varphi \leq 2\pi, \end{aligned}$$

the equation for the one-electron two-center problem after multiplying both sides by $\frac{1}{4}R^2(\lambda^2 - \mu^2)$ becomes

$$\begin{aligned} &\left[\frac{\partial}{\partial \lambda} \left((\lambda^2 - 1) \frac{\partial}{\partial \lambda} \right) + \frac{\partial}{\partial \mu} \left((1 - \mu^2) \frac{\partial}{\partial \mu} \right) \right. \\ &+ \left(\frac{1}{\lambda^2 - 1} + \frac{1}{1 - \mu^2} \right) \frac{\partial^2}{\partial \varphi^2} - p^2(\lambda^2 - \mu^2) + R(Z_A + Z_B)\lambda \\ &\left. - R(Z_A - Z_B)\mu + \frac{1}{4}R^2(\lambda^2 - \mu^2)V(\lambda, \mu, \varphi) \right] \psi(\lambda, \mu, \varphi) = 0, \end{aligned} \quad (2)$$

where $p^2 = -\frac{1}{2}ER^2$. As pointed out before (see paper I), when introducing a cylindrically symmetrical potential^{1,5-7} of the general form

$$V(\lambda, \mu) = [4/R^2(\lambda^2 - \mu^2)][f(\lambda) + g(\mu)], \quad (3)$$

the wave function $\psi(\lambda, \mu, \varphi)$ remains capable of being factorized, i.e., the solution of Eq. (2) can be written

$$\psi(\lambda, \mu, \varphi) = \Lambda(\lambda)M(\mu, \varphi) = \Lambda(\lambda)G(\mu)e^{+im\varphi},$$

where $\Lambda(\lambda)$ and $M(\mu, \varphi)$ are solutions of the following pair of differential equations:

$$\left[\frac{\partial}{\partial \mu} \left((1 - \mu^2) \frac{\partial}{\partial \mu} \right) - \frac{m^2}{1 - \mu^2} + p^2 \mu^2 - R(Z_A - Z_B)\mu - A - g(\mu) \right] M(\mu, \varphi) = 0, \quad (4)$$

$$\left[\frac{\partial}{\partial \lambda} \left((\lambda^2 - 1) \frac{\partial}{\partial \lambda} \right) - \frac{m^2}{\lambda^2 - 1} - p^2 \lambda^2 + R(Z_A + Z_B)\lambda + A - f(\lambda) \right] \Lambda(\lambda) = 0. \quad (5)$$

The separation constant A is the eigenvalue of the invariant operator⁷

$$\mathcal{G} = -L^2 - \frac{R^2}{4} \left(\Delta - \frac{\partial^2}{\partial Z^2} \right) - R(Z_A \cos \theta_A - Z_B \cos \theta_B) + \frac{R^2}{2} \left(\frac{(1 - \mu^2)f(\lambda) - (\lambda^2 - 1)g(\mu)}{\lambda^2 - \mu^2} \right) - p^2. \quad (6)$$

\vec{L} is the orbital angular momentum of the electron. At the limit $R=0$, \mathcal{G} still reduces to $-L^2$, and hereafter the united-atom labeling (n, l) is used.

In the present paper, we limit ourselves to consider a truncated expansion of $f(\lambda)$ and $g(\mu)$ up to the quadratic terms

$$\begin{aligned} f(\lambda) &= R(a_0 + a_1\lambda + a_2\lambda^2), \\ g(\mu) &= R(b_0 + b_1\mu + b_2\mu^2), \end{aligned} \quad (7)$$

where $a_0, a_1, a_2, b_0, b_1,$ and b_2 are parameters to be determined.

B. Determination of the parameters

In fact, without loss of generality, one can assume $b_0=0$ (or $a_0=0$) since, in the $V(\lambda, \mu)$ potential, the constant term is $R(a_0 + b_0)$. In the following sections we assume $b_0=0$. The determination of the remaining parameters $a_0, a_1, a_2, b_1,$ and b_2 could be performed either by considering limiting electrostatic cases of spatial configurations, or by a direct variational procedure. The screening method leads to values of the parameters which can be advantageously used as starting values for the variational procedure.

The former procedure has been first applied by Teller and Sahlin¹ for the H_2 molecule. We have extended it to the general homonuclear and heteronuclear two-center two-electrons problem. In both homonuclear and heteronuclear cases, the parameters are obtained by using symmetry properties and by considering two extreme situations: on one hand, the united-atom scheme with one electron at a great distance from the two nuclei; on the other hand, the separated-atom configura-

tion with one electron bound to one of the two atoms.

1. Homonuclear molecules ($Z_A = Z_B = Z$)

When assuming the particular form of the effective potential $V(\lambda, \mu)$ [Eqs. (3) and (7)], one gets the following expression of the total electrostatic potential $V_T(Z)$ of Eq. (2) in terms of the inter-particles distances (r_A, r_B, R):

$$\begin{aligned} V_T(Z) &= -2Z \left(\frac{1}{r_A} + \frac{1}{r_B} \right) + \frac{Ra_0}{r_A r_B} + a_1 \left(\frac{1}{r_A} + \frac{1}{r_B} \right) \\ &\quad + \frac{a_2}{R} \left(\frac{r_A}{r_B} + \frac{r_B}{r_A} + 2 \right) + b_1 \left(\frac{1}{r_B} - \frac{1}{r_A} \right) \\ &\quad + \frac{b_2}{R} \left(\frac{r_A}{r_B} + \frac{r_B}{r_A} - 2 \right). \end{aligned} \quad (8)$$

Since we are dealing with a homonuclear molecule, we must require the total potential to be symmetric with respect to reflection in a plane that is perpendicular to the molecular axis at its mid-point; hence we must select b_1 to be zero.

Let us consider the successive limiting cases. First, within the united-atom scheme, we assume that the electron "1" under consideration is far away from the nuclei ($r_A \sim r_B \gg R$) and also from the other electron "2". When replacing r_A by the following expression (see Fig. 1),

$$r_A = r_B \left[1 + \frac{2R}{r_B} \cos \theta_B + \left(\frac{R}{r_B} \right)^2 \right]^{1/2}, \quad (9)$$

and, after expanding the total electrostatic potential in ascending powers of (R/r_B) , ($R \ll r_B$) and retaining only the first two terms, it is easy to show that it must classically be

$$[V_C(Z)]_{\text{unit}} = \frac{1}{r_B} \left[-2(2Z - 1) + \left(\frac{R}{r_B} \right) 2(Z - 1) \cos \theta_B + \dots \right]. \quad (10)$$

From Eq. (8), one gets the following corresponding limit of $V_T(Z)$:

$$[V_T(Z)]_{\text{unit}} = \frac{4a_2}{R} + \frac{1}{r_B} \left[-2(2Z - a_1) + \left(\frac{R}{r_B} \right) [2(Z - 1) \cos \theta_B + a_0 + (2 - a_1) \cos \theta_B + (a_2 + b_2) \cos^2 \theta_B] + \dots \right]. \quad (11)$$

On the other hand, within the separated-atom scheme when the electron "1" under consideration is bound to nucleus B ($r_B \ll R$) while the other elec-

tron "2" is at a great distance ($r_A \sim R$) and near the other nucleus A, the potential of the electron classically becomes (see Fig. 2)

$$[V_C(Z)]_{\text{sep}} = -\frac{2Z}{r_B} - \frac{1}{R} \left[2(Z-1) - \left(\frac{r_B}{R}\right) 2(Z-1) \cos\theta_B + \dots \right], \quad (12)$$

where the expansion of

$$r_A = R \left[1 + \frac{2r_B}{R} \cos\theta_B + \left(\frac{r_B}{R}\right)^2 \right]^{1/2}$$

is used to obtain $[V_C(Z)]_{\text{sep}}$ expanded in power of (r_B/R) . Correspondingly, from Eq. (8) one gets

$$[V_T(Z)]_{\text{sep}} = \frac{1}{r_B} (-2Z + a_1 + a_2 + b_2 + a_0) - \frac{1}{R} \left[[2Z - a_1 + 2b_2 - 2a_2 - (a_2 + b_2 - a_0) \cos\theta_B] + \frac{r_B}{R} \left(\frac{a_0 - 3(a_2 + b_2)}{2} + (a_1 - 2Z) \cos\theta_B + \frac{a_2 + b_2 - 3a_0}{2} \cos^2\theta_B \right) + \dots \right]. \quad (13)$$

We must now satisfy pairwise the equality of the potential $V_C(Z)$ and $V_T(Z)$ for each limiting cases. First, for the united-atom limit ($R \ll r_A \sim r_B$), in order to satisfy the equality of potentials (10) and (11) one must require foremost

$$a_2 = 0. \quad (14)$$

When comparing the expressions (10) and (11) as

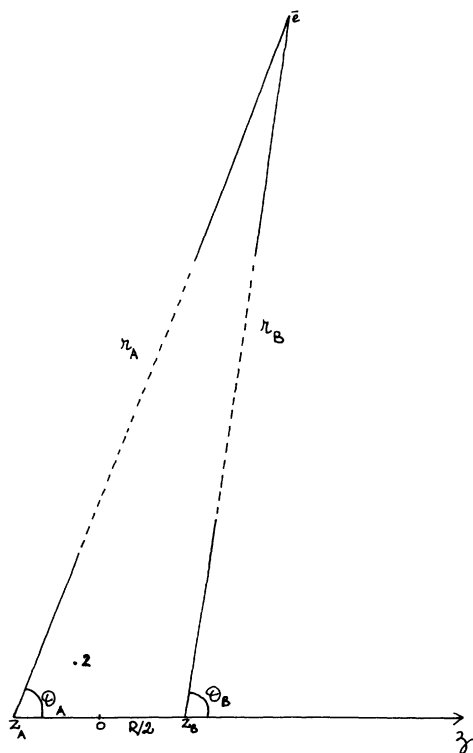


FIG. 1. United-atom scheme.

well as the expressions (12) and (13), we must first satisfy the equality of the predominant terms and we obtain the following conditions to be satisfied:

$$a_1 = 1, \quad (15)$$

$$a_1 + a_2 + b_2 + a_0 = 0.$$

Let us consider once more the effective separated-atom potential (13). Taking into account the conditions (14) and (15), it becomes

$$[V_T(Z)]_{\text{sep}} = -\frac{2Z}{r_B} - \frac{1}{R} [2(Z-1) + (2a_0 + a_1) (\cos\theta_B - 1) + \dots], \quad (16)$$

and consequently the second term of (16) will be equal, for any value of θ_B , to the term $2(Z-1)/R$ of the classical separated-atom limit [see Eq. (12)] when assuming

$$2a_0 + a_1 = 0. \quad (17)$$

Finally, from Eqs. (14), (15), and (17), one gets for the homonuclear case, the following empirical values of the parameters

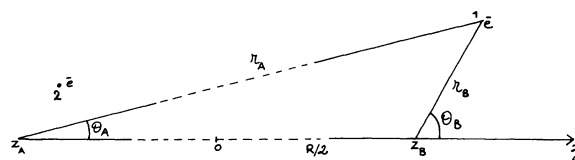


FIG. 2. Separated-atom scheme.

$$\begin{aligned} a_0 &= -\frac{1}{2}, \quad a_1 = 1, \quad a_2 = 0; \\ b_0 &= 0, \quad b_1 = 0, \quad b_2 = -\frac{1}{2}. \end{aligned} \quad (18)$$

It should be noted that these values of the parameters enable one to exactly equate only the first two terms (in $1/r_B$ and $1/R$) of the classical limit potential V_C with those of the effective limit poten-

tial V_T . Thus the effective potential to be considered is

$$V(\lambda, \mu) = [4/R^2(\lambda^2 - \mu^2)](-\frac{1}{2}R + R\lambda - \frac{1}{2}R\mu^2). \quad (19)$$

2. Heteronuclear molecules ($Z_A \neq Z_B$)

One gets the following expression of the total electrostatic potential:

$$V_T(Z_A, Z_B) = -\frac{2Z_A}{r_A} - \frac{2Z_B}{r_B} + \frac{Ra_0}{r_A r_B} + a_1 \left(\frac{1}{r_A} + \frac{1}{r_B} \right) + \frac{a_2}{R} \left(\frac{r_A}{r_B} + \frac{r_B}{r_A} + 2 \right) + b_1 \left(\frac{1}{r_B} - \frac{1}{r_A} \right) + \frac{b_2}{R} \left(\frac{r_A}{r_B} + \frac{r_B}{r_A} - 2 \right). \quad (20)$$

First, within the united-atom scheme ($r_A \sim r_B \gg R$), in the same way as for the homonuclear case, one obtains the following expression of the classical electrostatic potential for the electron "1" under consideration⁸:

$$[V_C(Z_A, Z_B)]_{\text{unit}} = \frac{1}{r_B} \left[-2(Z_A + Z_B - 1) + \left(\frac{R}{r_B} \right) 2(Z_A - 1) \cos \theta_B + \dots \right]. \quad (21)$$

From (20), one gets the following corresponding limit of $V_T(Z_A, Z_B)$:

$$\begin{aligned} [V_T(Z_A, Z_B)]_{\text{unit}} &= \frac{4a_2}{R} + \frac{1}{r_B} \left[-2(Z_A + Z_B - a_1) + \left(\frac{R}{r_B} \right) [2(Z_A - 1) \cos \theta_B \right. \\ &\quad \left. + a_0 + (a_2 + b_2) \cos^2 \theta_B - (a_1 - b_1 - 2) \cos \theta_B] + \dots \right]. \end{aligned} \quad (22)$$

Within the separated-atom limit we now consider the following spatial configuration, where the electron "1" under consideration is bound to one nucleus, for instance B , while the other electron "2" is at a great distance and near the other nucleus ($r_B \ll R \sim r_A$). The potential that feels the electron is classically

$$[V_C(Z_A, Z_B)]_{\text{sep}} = -\frac{2Z_B}{r_B} - \frac{1}{R} \left[2(Z_A - 1) - \left(\frac{r_B}{R} \right) 2(Z_A - 1) \cos \theta_B + \dots \right]. \quad (23)$$

From (20), one gets the corresponding limit of $V_T(Z_A, Z_B)$:

$$\begin{aligned} [V_T(Z_A, Z_B)]_{\text{sep}} &= \frac{1}{r_B} (-2Z_B + a_0 + a_1 + a_2 + b_1 + b_2) - \frac{1}{R} \left[2(Z_A - 1) + 2b_2 - 2a_2 + b_1 - a_1 + 2 - (a_2 + b_2 - a_0) \cos \theta_B \right. \\ &\quad \left. + \left(\frac{r_B}{R} \right) \left(\frac{a_0 - 3(a_2 + b_2)}{2} + (a_1 - b_1 - 2Z_A) \cos \theta_B \right. \right. \\ &\quad \left. \left. + \frac{a_2 + b_2 - 3a_0}{2} \cos^2 \theta_B \right) + \dots \right]. \end{aligned} \quad (24)$$

We must now satisfy pairwise the equality of the potential $V_C(Z_A, Z_B)$ and $V_T(Z_A, Z_B)$ for each limiting case. First, from the united-atom limit, one must require foremost

$$a_2 = 0. \quad (25)$$

When comparing the expressions (21) and (22), as well as the expressions (23) and (24), we must first satisfy the equality of the predominant terms,

and we obtain the following conditions to be satisfied:

$$\begin{aligned} a_1 &= 1, \\ a_0 + a_1 + a_2 + b_1 + b_2 &= 0. \end{aligned} \quad (26)$$

Let us now consider once more the effective separated-atom potential (24). Taking into account the conditions (25) and (26), it becomes

$$[V_T(Z_A, Z_B)]_{\text{sep}} = -\frac{2Z_B}{r_B} - \frac{1}{R} \left[2(Z_A - 1) - (2a_0 + a_1 + b_1)(1 - \cos \theta_B) + \dots \right]. \quad (27)$$

Consequently, when assuming that

$$2a_0 + a_1 + b_1 = 0, \quad (28)$$

the first two terms of the potentials $[V_C(Z_A, Z_B)]_{\text{sep}}$ and $[V_T(Z_A, Z_B)]_{\text{sep}}$ become equal for any value of θ_B . One easily obtains the conditions corresponding to the alternative situation where the electron under consideration is bound to the nucleus A , by interchanging A and B in the relations (23), (24), and (27), i.e.,

$$a_0 + a_1 + a_2 - b_1 + b_2 = 0, \quad (29)$$

$$2a_0 + a_1 - b_1 = 0.$$

Finally, from Eqs. (25), (26), (28), and (29) one gets, for the heteronuclear case, the same empirical potential [Eq. (19)] as for the homonuclear case. This is not very surprising, owing to the fact that we have considered only limiting cases which are symmetrical when interchanging nucleus A and B . Other possible situations of the separated-atoms scheme, such as the two electrons bound to the same nucleus, have not been taken into account. Their eventual influence on the determination of the parameters will be discussed in Sec. IV.

III. CALCULATIONS

For both homonuclear and heteronuclear cases, the empirical potential $V(\lambda, \mu)$ [Eq. (19)] is linear in λ ($a_2 = 0$) and quadratic in μ ; this corresponds to the additional potential we have previously considered [see Eqs. (14) and (15) of paper I]. Furthermore, the construction process for the shielded diatomic (SDO) orbitals has been described in this paper. Hereafter the same nota-

TABLE IA. DO and SDO (1σ) orbital of the H_2 molecule ($R_e = 1.4$ a.u.).

Orbital 1σ Type of calculation	SDO		
	DO Without screening	Empirical screening	Variational screening
A	0.443 890 32	0.507 420 73	0.465 684 35
p	1.121 866 24	0.853 093 34	0.795 595 29
$M(\mu, \varphi)$ Coefficients	f_0	0.997 898	0.997 273
	f_2	0.064 790	0.073 793
	f_4	0.001 052	0.001 361
	f_6	0.000 008	0.000 012
$\Lambda(\lambda)$ Coefficients	C_0	0.999 094	0.999 426
	C_1	-0.042 334	0.033 364
	C_2	-0.004 252	0.005 682
	C_3	-0.000 824	0.001 474
	C_4	-0.000 216	0.000 477
	C_5	-0.000 068	0.000 177
	C_6	-0.000 024	0.000 073
	C_7	-0.000 009	0.000 032
	C_8	-0.000 004	0.000 014
$\langle V \rangle$	0	0.527 96	0.609 48
$\langle 1/r_{12} \rangle$	0.780 88	0.700 33	0.663 50

TABLE IB. DO and SDO (1σ) orbital of the He_2^{2+} molecular ion ($R_e = 1.3$ a.u.).

Orbital 1σ Type of calculation	SDO		
	DO Without screening	Empirical screening	Variational screening
A	1.274 333 95	1.314 715 41	1.282 997 51
p	1.815 768 76	1.654 644 32	1.566 296 57
$M(\mu, \varphi)$ Coefficients	f_0	0.984 435	0.983 531
	f_2	0.175 588	0.180 562
	f_4	0.007 553	0.007 983
	f_6	0.000 151	0.000 164
$\Lambda(\lambda)$ Coefficients	C_0	0.998 663	0.999 757
	C_1	-0.051 608	-0.021 955
	C_2	-0.002 904	-0.001 835
	C_3	-0.000 388	-0.000 292
	C_4	-0.000 075	-0.000 063
	C_5	-0.000 018	-0.000 017
	C_6	-0.000 005	-0.000 005
	C_7	-0.000 002	-0.000 002
$\langle V \rangle$	0	0.658 92	0.981 14
$\langle 1/r_{12} \rangle$	1.153 63	1.125 17	1.081 82

tions will be used. The eigenfunction $M(\mu, \varphi)$ of Eq. (4) is expanded as a linear combination of spherical harmonics:

$$M(\mu, \varphi) = \sum_{k=m}^{\infty} f_k^m Y_k^m(\mu, \varphi), \quad (30)$$

where, for the heteronuclear case ($Z_A \neq Z_B$) all the consecutive integer values of k are to be con-

TABLE IC. DO and SDO (1σ) orbital of the HeH^+ molecular ion ($R_e = 1.4$ a.u.).

Orbital 1σ Type of calculation	SDO		
	DO Without screening	Empirical screening	Variational screening
A	1.454 085 54	1.539 758 93	1.210 205 02
p	1.640 805 21	1.450 527 29	1.335 064 78
$M(\mu, \varphi)$ Coefficients	f_0	0.870 600	0.867 035
	f_1	0.458 306	0.462 870
	f_2	0.174 806	0.180 017
	f_3	0.037 419	0.039 151
	f_4	0.007 330	0.007 828
	f_5	0.001 021	0.001 109
	f_6	0.000 135	0.000 150
	f_7	0.000 014	0.000 016
$\Lambda(\lambda)$ Coefficients	C_0	0.999 370	0.999 989
	C_1	-0.035 378	0.004 558
	C_2	-0.002 650	0.000 507
	C_3	-0.000 406	0.000 095
	C_4	-0.000 086	0.000 023
	C_5	-0.000 022	0.000 007
	C_6	-0.000 007	0.000 002
	C_7	-0.000 002	
$\langle V \rangle$	0	0.596 50	0.886 15
$\langle 1/r_{12} \rangle$	1.232 25	1.197 06	1.054 14

TABLE IIA. Variation with R of the total energy E_T (in a.u.) of the H_2 molecule.^a

R	$-E_T$ (1)	$-E_T$ (2)	$-E_T$ (3)	$-E_T$ (4)	$-E_T$ (5)	V (3)	$\left\langle \frac{1}{r_{12}} \right\rangle$ (3)
1.30	1.069 21	1.126 35	1.131 33	1.131 36	1.131 43	0.637 45	0.677 23
1.32	1.070 43	1.126 75	1.132 05	1.132 08	1.132 12	0.631 67	0.674 47
1.34	1.071 45	1.126 97	1.132 59	1.132 59	1.132 60	0.625 99	0.671 72
1.36	1.072 27	1.127 00	1.132 88		1.132 90	0.620 39	0.668 98
1.38	1.072 90	1.126 85		1.133 02	1.133 02	0.614 89	0.666 23
1.40	1.073 37	1.126 55	1.132 96	1.132 97	1.132 96	0.609 48	0.663 50
1.42	1.073 68	1.126 10	1.132 75	1.132 76	1.132 78	0.604 16	0.660 77
1.44	1.073 83	1.125 51		1.132 39	1.132 44	0.598 93	0.658 04
1.46	1.073 86	1.124 79	1.131 88	1.131 189	1.131 96	0.593 78	0.655 33
1.48	1.073 81	1.123 96		1.131 25	1.131 35	0.588 72	0.652 62
1.50	1.073 74	1.123 00		1.130 49	1.130 63	0.583 73	0.649 92
R_e	1.452	1.353	1.384	1.384	1.384		
k_e	0.3366	0.4374	0.4241	0.4283	0.4020		

^a (1) Without screening; (2) empirical screening; (3) variational screening; (4) variational screening with a truncated basis; (5) reoptimized calculation.

sidered, whereas for the homonuclear case the values of k jump by steps of two units.

For the $\Lambda(\lambda)$ eigenfunction of Eq. (5), we have chosen an Hylleraas-like expansion⁹

$$\Lambda(\lambda) = e^{-p(\lambda-1)} [2p(\lambda-1)]^{m/2} \times \sum_{n=m/2}^{\infty} C_{n-m/2} \mathcal{L}_{n-m/2}^m [2p(\lambda-1)], \quad (31)$$

where the quantity $n - (m/2)$ is an integer and $\mathcal{L}_n^m(x)$ is the normalized associated Laguerre polynomial. The values of the unshielded parameters A and p are used to initialize the Newton-Raphson procedure.

In order to calculate the electronic energy, we have computed the Coulombic repulsion integral $\langle 1/r_{12} \rangle$ by a seminumerical technique (see Appendix D of paper I) very similar to the technique of Wahl *et al.*¹⁰ The one-electron energy is calculated by difference, i.e.,

$$\langle \psi | \Delta + 2 \left(\frac{Z_A}{r_A} + \frac{Z_B}{r_B} \right) | \psi \rangle = \frac{2p^2}{R^2} - \langle \psi | V(\lambda, \mu) | \psi \rangle. \quad (32)$$

ψ is assumed to be normalized. The normalization integral as well as the $\langle V \rangle$ integral in Eq. (32) are calculated analytically (see Appendix D of paper I).

Three types of calculation (noted hereafter i, ii,

TABLE IIB. Variation with R of the total energy E_T (in a.u.) of the He_2^{2+} molecular ion.^a

R	$-E_T$ (1)	$-E_T$ (2)	$-E_T$ (3)	$-E_T$ (4)	$-E_T$ (5)	V (3)	$\left\langle \frac{1}{r_{12}} \right\rangle$ (3)
1.20	3.568 26	3.594 03	3.608 14	3.608 15	3.608 14	1.039 46	1.124 92
1.22	3.570 36	3.595 50	3.609 66	3.609 67	3.609 66	1.027 20	1.115 97
1.24	3.571 83	3.596 37	3.610 57	3.610 58	3.610 57	1.015 24	1.110 72
1.26	3.572 74	3.596 69	3.610 92	3.610 93	3.610 92	1.003 59	1.098 57
1.28	3.573 13	3.596 51	3.610 76	3.610 77	3.610 76	0.992 23	1.090 12
1.30	3.573 04	3.595 86	3.610 13	3.610 14	3.610 13	0.981 14	1.081 82
1.32	3.572 52	3.594 80	3.609 07	3.609 09	3.609 09	0.970 33	1.073 68
1.34	3.571 59	3.593 36	3.607 63	3.607 65	3.607 65	0.959 77	1.065 69
1.36	3.570 31	3.591 47	3.605 84	3.605 85	3.605 86	0.949 47	1.057 85
1.38	3.568 69	3.589 45	3.603 72	3.603 73	3.603 76	0.939 41	1.050 15
1.40	3.566 77	3.587 06	3.601 31	3.601 32	3.601 37	0.929 58	1.042 60
R_e	1.286	1.262	1.263	1.263	1.263		
k_e	1.1380	1.2424	1.2592	1.2580	1.2564		

^a (1) Without screening; (2) empirical screening; (3) variational screening; (4) variational screening with a truncated basis; (5) reoptimized calculation.

TABLE IIC. Variation with R of the total energy E_T (in a.u.) of the HeH^+ molecular ion.^a

R	$-E_T$ (1)	$-E_T$ (2)	$-E_T$ (3)	$-E_T$ (4)	$-E_T$ (5)	V (3)	$\left\langle \frac{1}{r_{12}} \right\rangle$ (3)
1.22	2.829 08	2.863 46					
1.24	2.830 70	2.864 26					
1.26	2.831 99	2.864 73					
1.28	2.832 96	2.864 92					
1.30	2.833 64	2.864 85	2.923 18	2.923 17	2.923 30	0.917 42	1.062 40
1.32	2.834 06	2.864 53	2.924 43	2.924 42	2.924 50	0.910 80	1.060 46
1.34	2.834 24	2.864 00	2.925 44	2.925 42	2.925 46	0.904 38	1.058 67
1.36	2.834 20	2.863 27	2.926 21	2.926 19	2.926 21	0.898 13	1.057 02
1.38	2.833 96	2.862 37	2.926 77	2.926 75	2.926 77	0.892 06	1.055 51
1.40	2.833 54	2.861 31	2.927 13	2.927 12	2.927 13	0.886 15	1.054 14
1.42	2.832 97	2.860 11	2.927 32	2.927 30	2.927 35	0.880 41	1.052 91
1.44	2.832 24	2.858 78	2.927 34	2.927 32	2.927 42	0.874 82	1.051 80
1.46	2.831 38	2.857 34	2.927 21	2.927 19	2.927 33	0.869 38	1.050 83
1.48	2.830 41	2.855 50	2.926 94	2.926 91	2.927 18	0.864 08	1.049 97
1.50	2.829 33	2.854 18	2.926 54	2.926 51	2.926 84	0.858 93	1.049 24
R_e	1.346	1.284	1.433	1.432	1.440		
k_e	0.5302	0.6464	0.3916	0.3938	0.3361		

^a (1) Without screening; (2) empirical screening; (3) variational screening; (4) variational screening with a truncated basis; (5) reoptimized calculation.

and iii) of the ground-state energy and wave function for the $(1\sigma)^2$ configuration at various internuclear distances have been carried out for H_2 , He_2^{2+} , and HeH^+ molecule and molecular ions:

(i) without introducing the screening potential $V(\lambda, \mu)$; (ii) taking into account the screening potential [Eq. (19)] corresponding to the empirical values of the parameters; and (iii) taking into account a screening potential, linear in λ and quadratic in μ , the parameters of which are determined by variation, using a steepest-descent procedure.

For each case, the equilibrium distance R_e and the force constant k_e have been obtained by a least-squares polynomial fit of the energy (12 points and degree 4).

IV. RESULTS AND DISCUSSION

For each molecule or molecular ion (H_2 , He_2^{2+} , and HeH^+), the results concerning the 1σ diatomic orbital are comparatively displayed for the three types of calculation. The values of A and p (in a.u.), the expansion coefficients f_i and C_i [see Eq. (30) and (31)], as well as the values of the electronic integrals, near the presumed value of the internuclear distance R_e , are given in Table IA-IC.

For each type of calculation already described, we have computed the total energy E_T (in a.u.) for several internuclear distances round the minimum (Table II). Since the expansion coefficients appear

to be rapidly decreasing, we repeated the calculation when neglecting the coefficients less than 10^{-3} . These last results [noted (4)] are seen to be very close to the more elaborate ones (3).

Although the screening potential is R dependent [Eq. (7)], the values of its parameters a_i and b_i , which are independent of R within the empirical scheme, are found to be still quasi-independent of R when determined variationally. This allows the transferability, for all internuclear distances R , of the potential parameters a_i and b_i , which, consequently are to be calculated only once. Nevertheless, this transferability property has been fairly checked by reoptimizing the total energy E_T at each internuclear distance R [results noted (5) in Table II].

TABLE IIIA. Potential parameters of the H_2 molecule.

Empirical values	R	a_0 -0.500	a_1 1.000	b_2 -0.500
Variational values	1.30	-0.454	1.059	-0.492
	1.32	-0.453	1.061	-0.493
	1.34	-0.447	1.066	-0.491
	1.36	-0.447	1.066	-0.491
	1.38	-0.447	1.066	-0.491
	1.40	-0.447	1.066	-0.491
	1.42	-0.444	1.071	-0.491
	1.44	-0.442	1.073	-0.490
	1.46	-0.439	1.076	-0.490
	1.48	-0.437	1.078	-0.489
	1.50	-0.435	1.078	-0.487

TABLE IIIB. Potential parameters of the He_2^{2+} molecular ion.

	R	a_0	a_1	b_2
Empirical values		-0.500	1.000	-0.500
Variational values	1.20	-0.295	1.134	-0.664
	1.22	-0.295	1.134	-0.664
	1.24	-0.295	1.134	-0.664
	1.26	-0.295	1.134	-0.664
	1.28	-0.295	1.134	-0.664
	1.30	-0.295	1.134	-0.664
	1.32	-0.294	1.136	-0.666
	1.34	-0.293	1.137	-0.666
	1.36	-0.292	1.137	-0.666
	1.38	-0.291	1.139	-0.668
	1.40	-0.289	1.140	-0.671

Although the optimized values of the parameters a_0 , a_1 , and b_2 remain close to their empirical values, and vary very slowly with R (Table III), the energy E_T is very sensitive to their variation, as can be seen from comparison of the results (2) and (3) of Table II.

For the HeH^+ molecular ion (see Table IIIC), the empirical value of b_1 is zero, whereas this is not the case when obtained by variation. This can be explained by remembering that in our electrostatic considerations we have not introduced non-symmetrical electrostatic situations; for instance, within the separated-atom scheme, we have not introduced the possibility for the two electrons to be both on the same nucleus (for instance B). For that case, the limit of $V_T(Z_A, Z_B)$ is still given by Eq. (24), whereas the classical potential that feels the electron under consideration becomes

TABLE IIIC. Potential parameters of the HeH^+ molecular ion.

	R	a_0	a_1	b_2	b_1
Empirical values		-0.500	1.000	-0.500	0.000
Variational values	1.30	-0.424	1.096	-0.557	0.282
	1.32	-0.423	1.097	-0.556	0.284
	1.34	-0.422	1.098	-0.556	0.286
	1.36	-0.419	1.100	-0.551	0.293
	1.38	-0.419	1.100	-0.551	0.296
	1.40	-0.419	1.100	-0.551	0.296
	1.42	-0.420	1.102	-0.554	0.296
	1.44	-0.418	1.103	-0.552	0.300
	1.46	-0.417	1.105	-0.551	0.304
	1.48	-0.421	1.104	-0.557	0.307
	1.50	-0.420	1.103	-0.557	0.310

$$[V_C(Z_A, Z_B)]_{\text{sep}} = \frac{-2(Z_B - \sigma)}{r_B} - \frac{1}{R} \left[2Z_A - \left(\frac{r_B}{R} \right) 2Z_A \cos \theta_B + \dots \right], \quad (33)$$

where σ is the atomic screening of the inner electron. In order to satisfy the equality of the first term of the potential $[V_C(Z_A, Z_B)]_{\text{sep}}$ and $[V_T(Z_A, Z_B)]_{\text{sep}}$ [Eq. (24)], the following condition is to be satisfied:

$$a_0 + a_1 + a_2 + b_1 + b_2 = 2\sigma. \quad (34)$$

Taking into account the strong condition $a_2 = 0$ [Eq. (25)] and the condition previously determined, and also corroborated by the variational results [see Table IIIC], $a_0 + a_1 + b_2 = 0$;

TABLE IV. Some comparative results (in a.u.).

	$-\mathcal{E}_T$	H_2 R_e	k_e	He_2^{2+} $-\mathcal{E}_T$	R_e	$-\mathcal{E}_T$	HeH^+ R_e	k_e
	1.128 06 ^a							
	1.127 64 ^b							
	1.133 60 ^c			3.6091 ^c				
Present work	1.133 02	1.384	0.4020	3.610 93	1.263	2.927 42	1.440	0.3361
SCF	1.133 642 ^d	1.375 ^d	...	3.611 180 ^d	1.3	2.933 93 ^e	1.455 ^e	0.3193 ^e
Best value	1.174 475 ^f	1.4006 ^g	0.3692 ^h	3.679 845 ^d	1.32	2.978 67 ⁱ	1.4632 ⁱ	

^a See Ref. 3.^b See Ref. 2.^c S. M. Rothstein (private communication); C. T. Llaguno, S. K. Gupta, and S. M. Rothstein, Intern. J. Quantum Chem. **7**, 819 (1973).^d W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).^e S. Peyerimhoff, J. Chem. Phys. **43**, 998 (1965).^f W. Kolos and L. Wolniewicz, J. Chem. Phys. **49**, 404 (1968).^g G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 636 (1959).^h B. P. Stoicheff, Can. J. Phys. **35**, 730 (1957).ⁱ L. Wolniewicz, J. Chem. Phys. **43**, 1087 (1965).

TABLE V. Values of the virial ratio $\langle E_T/E_{\text{pot}} \rangle_{R_e}$.

	Without screening	Empirical screening	Variational screening	Expected value
H ₂	0.4159	0.4669	0.4991	
He ₂ ²⁺	0.4652	0.4757	0.4997	0.5
HeH ⁺	0.4165	0.4322	0.4984	

when solving the remaining equations [(26), (29), and (34)] by a least-squares method, one obtains

$$b_1 = \sigma.$$

This result appears consistent with the optimized result, since from Slater's rules $\sigma = 0.30$ [see Table III C].

The introduction in $V(\lambda, \mu)$ [Eq. (7)] of polynomials $f(\lambda)$ and $g(\mu)$ of higher degree in λ and μ does not result in special technical difficulties: the method remains valid, but one must deal with slightly larger band matrices. Nevertheless, in this last case, in order to determine the empirical values of all the parameters a_i and b_i , we would have to take into account other possible limiting electrostatic situations which have not all the same weight of importance. On the other hand, the determination of these parameters by optimization would be equivalent, at the limit, to an analytical separable Hartree-Fock calculation.¹ Our results, which correspond to a two-variables pre-Hartree-Fock calculation introducing a part of both angular and radial correlation when the potential parameters are optimized, are not too far from the Hartree-Fock limit.

The corresponding values of the equilibrium distance R_e and of the force constant k_e are in good agreement with the self-consistent-field (SCF) values (see Table IV). In order to test the quality of the wave function, we have applied the virial theorem, i.e.,

$$\langle E_{\text{pot.}} \rangle = 2\langle E_T \rangle + R \left(\frac{\partial \langle E_T \rangle}{\partial R} \right),$$

where $\langle E_{\text{pot.}} \rangle$ is the value of the total potential en-

ergy. Since at the equilibrium distance R_e , the derivative term vanishes, one should expect that

$$\langle E_T \rangle / \langle E_{\text{pot.}} \rangle_{R_e} = \frac{1}{2}.$$

For the three types of calculation, the values of this last ratio are given in Table V and it is seen that the introduction of screening effects goes with a better fulfillment of the virial theorem. Our results are gratifying in view of the fact that we have limited ourselves to an expansion of the effective potential which is linear in λ and quadratic in μ .

As a matter of curiosity, using our program for $Z_A = 0$ and $Z_B = 2$ (or $Z_A = 2$ and $Z_B = 0$), we obtained the diatomic orbitals 1S of the helium atom which are no longer eigenfunctions of L^2 but eigenfunctions of the operators α [Eq. (6)] and L_z . Results are given in Table VI.

V. CONCLUSION

We have determined both empirically and variationally the SDO for two electrons systems in their ground state and have found that these SDO are, in some respects, comparable to the SCF orbitals. Furthermore, the screening parameters are independent of the internuclear distance, and consequently such SDO can be advantageously used as basis orbitals in molecular calculations. Nevertheless, when extending the method to N -electrons diatomic molecules, the empirical procedure becomes more involved, owing to the fact that many limiting possible electrostatic situations can be considered and it is rather difficult to weight their relative importance. On the other hand, the variational determination of the effective potential does not involve further difficulties when one assumes the additivity of the screening effects and determines the successive SDO, from the inner shells to the outer shell: Once the $(N-1)$ inner SDO are known, the determination of the outer N th can be performed in the same way as for the two-electrons case. Such an extension, as well as others and calculations of molecular properties with the SDO will be given in a forthcoming paper.

TABLE VI. Total energy of atomic helium ground state $(1\sigma)^2$ (in a.u.).

	Diatomic scheme	Atomic scheme
Without screening (1)	-2.75	-2.75 (Hydrogenics)
Empirical screening (2)	-2.8168	-2.8475 (Slater's orbitals)
Variational screening (3)	-2.8547	-2.86168 (SCF orbitals)

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