

State-specific theory and method for the computation of diatomic molecules: Application to $\text{He}_2^{2+} \ ^1\Sigma_g^+$

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We present a state-specific approach to the calculation of correlated wave-functions and potential-energy surfaces (PES's) of ground and excited states of diatomic molecules. Its emphasis is on the optimal choice of zeroth-order and of correlation-function spaces, which are computed separately. The zeroth-order Fermi-sea multiconfigurational wave function is obtained numerically, using McCullough's partial-wave multiconfiguration self-consistent field [Comput. Phys. Rep. **4**, 265 (1986)] program PWMSCF and numerical one-electron two-center orbitals as input. The correlation functions are obtained from partial and total configuration interaction (CI), using two-center virtual molecular orbitals, optimized by minimizing the energy. The method is demonstrated on the prototype $\text{He}_2^{2+} \ ^1\Sigma_g^+$. A number of wave functions of ascending accuracy have been calculated. The most accurate one is composed of 116 configurations (multiconfiguration Hartree-Fock plus higher-order correlations), arising from 43 orbitals. It yields results which are lower over the entire PES than those obtained from the conventional linear combination of atomic orbitals including full CI with 158 basis functions and 2282 configurations. Compared with a published large CI calculation with r_{ij} -dependent basis sets, only at the equilibrium position, where the influence of the Coulomb cusp increases, does the present approach yield a slightly (4×10^{-4} a.u.) higher energy. For the rest of the PES, our calculation yields the lowest energies yet.

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I. INTRODUCTION

The widely used approaches to advanced quantum chemical calculations, such as full or hierarchical configuration-interaction (CI), multiconfiguration self-consistent-field (MCSCF), coupled-cluster and perturbation expansions, have a common characteristic: They are implemented in terms of the linear combination of atomic orbitals (LCAO) concept, where the atomic-orbital (AO) basis sets are common to the zeroth and the virtual N -electron spaces. This fact refers not only to the treatment of the ground state—where, in general, electron correlations are more easily understood—but also to low-lying excited states (if the formalism and method are truly applicable there).

The prescription of an AO input common to the zeroth order and virtual symmetry-adapted spaces facilitates the construction of formalism as well as of related computational algorithms. On the other hand, such approaches contain intrinsic limits of accuracy and efficiency, since the N -electron function spaces which they utilize are not optimal. Thus, although it is expected that by enlarging the basis sets the reliability of results increases, it is well known that in practice, when high accuracy is desired, very quickly a law of diminishing returns sets in, even with today's supercomputers. Furthermore, spectroscopically and chemically significant situations, such as avoided intersections and valence-Rydberg-scattering (VRS) mixing, depend crucially on the accuracy of the zeroth-order radial description, regardless of the overall size of the computation, and it is not clear how to improve the

accuracy via the adjustment of the input of AO basis sets. Finally, because the wave functions resulting from such computations are very large, it is often impossible to depend on their use for the quantitative treatment of phenomena involving more than one state, such as multichannel scattering or laser-induced nonlinear effects.

In the state-specific theory (SST) of electronic structure and properties [1–4], where the formalism includes the continuous spectrum, emphasis has been given to the determination of optimal as well as practical one-electron and N -electron function spaces for the zeroth-order representation and for the correlation correction, for each state of interest. A large number of applications have been done. The extent of the full calculation and the choice of correlations that must be incorporated in it depend on the property which must be computed.

Here we present a method for the computation of electron correlation in diatomic molecules, which allows the implementation of the SST in a manner analogous to that which has been developed and applied over the years to atomic ground and low- or high-lying excited states [1–7]. As a test case, we chose the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state. In a separate paper we deal with the theory of excited states, and in particular with the *a priori* construction of correlated wave functions of diabatic states.

II. THEORETICAL FRAMEWORK

By definition, the exact fixed-nuclei electronic wave function Ψ of a particular ground or discrete excited

atomic or molecular state, can be written as

$$\Psi = a_0 \Phi_0 + \sum_n a_n \Phi_n, \quad (1a)$$

$$a_0^2 + \sum_n a_n^2 = 1, \quad \langle \Phi_0 | \Phi_n \rangle = 0. \quad (1b)$$

The separation of Ψ into two terms is directly related to the fundamental characteristic of a_0 : Given the symmetry of the state, its square is larger than 0.5, in which case Φ_0 can be called the “zeroth-order” wave function. The aim of a computationally oriented theory of electronic structure should be to start with a *radially optimal* Φ_0 for which a_0 is close to 1, while the size of Φ_0 is as compact as possible and its calculation takes only a fraction of the overall calculation of Ψ . This statement is equivalent to saying that the Φ_0 and Φ_n of Eq. (1) should be computed in such a way as to achieve convergence of the desired answer (quantitative or semiquantitative), reliably and without sacrificing simplicity or economy of effort.

Soon after the publication of Froese Fischer’s atomic numerical multiconfiguration Hartree-Fock (MCHF) computer code [8], Beck and Nicolaides [2,3] formulated and implemented a variational approach to the computation of Ψ based on the state-specific numerical MCHF Φ_0 , whose configurations were chosen according to the Fermi-sea (FS) concept [1–3]. The Fermi-sea is the set of zeroth-order spin orbitals that are deemed to be the most important for the state of interest. Thus

$$\Phi_0 = \sum_k a_k \Phi_0^k, \quad (1c)$$

where Φ_0^k are symmetry-adapted self-consistent-field (SCF) configurations with orbitals belonging to the Fermi-sea [9]. Guidelines for the choice of the FS orbitals were given as a combination of empirical with *a priori* rules [2,3]. As regards the computation of the single, double, triple, etc., symmetry-adapted correlation functions entering in Φ_n , these are obtained in terms of variationally optimized analytic virtual orbitals via nonorthonormal CI methods [1,2,7].

Thus, in Eq. (1), Φ_0 is composed of one or more configurations with numerical orbitals while the Φ_n contain numerical as well as analytic functions (representing the virtual orbitals). In this way, the radial details of the important zeroth-order orbitals are not lost (as they are when LCAO are used, especially in delicate situations such as valence-Rydberg or covalent-ionic mixing, properties of negative ions or of multiply excited states, etc.), while the correlation function spaces are manipulated and optimized with flexibility, whether the state of interest is ground or excited. This approach has been incorporated in a general theory and method of atomic spectroscopy which include the multichannel continuous spectrum, Rydberg series, and resonances [1,4].

The construction by McCullough [10] in the mid 1970s of the numerical MCHF program for diatomic molecules led to the expectation (Ref. [2], pp. 122 and 123) that SST methods similar to the atomic ones ought to be possible for diatomics. In other words, for each state of interest, a numerical self-consistently-optimized Φ_0 could

replace the AO-based zeroth-order function of the conventional methods, thereby reducing immediately an uncontrollable source of error. (For example, consider the difficulties of choosing systematically “diffuse” bases for the reliable calculation of negative ions, of nonlinear polarization or of highly excited states.) The remaining correlation would be adapted to the diatomic symmetry and computed variationally. The method that is presented in the next section shows how this can be accomplished.

III. METHOD OF CALCULATION

The calculation consists of two essential steps. (i) Construction of the optimal, multiconfigurational FS Φ_0 in terms of numerical diatomic orbitals: (ii) variational optimization of virtual orbitals for the construction of the higher-order terms Φ_n of the wave function.

A. Numerical zeroth order Φ_0

The problem of the appropriate initial guess is very crucial to the successful numerical computation of a desired MCHF wave function based on McCullough’s [11] partial-wave multiconfiguration self-consistent field program PWMCSF. The program requires the orbital input as a linear combination of Slater-type orbitals (STO’s). This approach may lead to much experimentation. Furthermore, from our experience on excited states, convergence to the correct state is often not achieved. Therefore, we have implemented a different approach where the input is taken from the solution of the one-electron diatomic molecule in prolate spheroidal coordinates.

1. Numerical orbital input to the MCHF procedure. Orbital nodes

In prolate spheroidal coordinates, the one-electron diatomic orbital (OEDO) is written as

$$\psi(\mathbf{r}) = \Xi(\xi)H(\eta)e^{\pm im\varphi}, \quad m=0,1,2,\dots \quad (2)$$

where $\mathbf{r}=(\xi,\eta,\varphi)$ is the position of the electron, $\xi=(r_a+r_b)/R$, $\eta=(r_a-r_b)/R$, φ is the azimuthal angle and r_a, r_b are the distances of the electron from the nuclei Z_a, Z_b , respectively, which are located on the z axis, a distance R apart.

We use Power’s quantum chemistry program exchange (QCPE) one-electron diatomic molecule program OEDM [12,13] to obtain the necessary information for the construction of the OEDO’s, as explained in the Appendix.

McCullough [11] also uses prolate spheroidal coordinates to expand the orbitals used in the many-electron wave function, which is a linear combination of Slater determinants, in a partial-wave expansion over η ,

$$\psi(\mathbf{r}) = \sum_{j=|m|}^{L_{\max}} X_j(\xi)Y_j^m(\eta,\varphi), \quad (3)$$

where $Y_j^m(\eta,\varphi)$ are spherical harmonics. Accordingly, we expand the OEDO’s in partial waves over η , thus con-

structuring our initial guesses to the MCHF, as explained in the Appendix.

Using OEDO's as input has the advantage, compared to the linear combinations of STO's (used originally by McCullough [11]), that one can use the conservation of the number of their nodes in order to lead convergence to the desired state, especially if it is excited. The OEDO's are customarily labeled by their united-atom-limit quantum numbers n , l , and m , where $l = s, p, d, \dots$ and $m = \sigma, \pi, \delta, \dots$, corresponding to the numerical values $0, 1, 2, \dots$, respectively. For homonuclear molecules the inversion symmetry is described by subscripts g for l even and u for l odd. They may also be characterized by the number of nodes (i.e., nonmultiple zeros) that they possess in each coordinate ξ, η, φ . Let n_ξ, n_η , and n_φ be the number of nodes of $\Xi(\xi)$, $H(\eta)$, and $\cos(m\varphi)$, or $\sin(m\varphi)$, respectively. As R varies, these node quantum numbers are conserved, except at infinite R , for heteronuclear diatomic molecules, where n_η is not necessarily conserved [12]. In terms of the united atom limit quantum numbers, $n_\xi = n - l - 1$, $n_\eta = l - m$, and $n_\varphi = m$. The conservation of the node quantum numbers can be used for the identification of the desired orbital during the SCF procedure. For a MCHF orbital the partial-wave functions $X_j(\xi)$ decrease uniformly, with increasing j , while the number of their nodes is not necessarily the same for all of them. However, the character of the orbital is mainly determined by the first one, $X_1(\xi)$, which usually does not significantly differ from the corresponding OEDO (this is especially true for a Rydberg state, where the orbital is almost purely one electron). Thus, it is possible to identify the MCHF orbital by counting the nodes of its first partial-wave component $X_1(\xi)$. In the Appendix we give some examples.

2. Choice and optimization of Φ_0^k [Eq. (1c)]

The choice of the form of Φ_0^k is made with the criteria presented in Sec. II. One might argue for as large a Φ_0 as possible. However, this is unnecessarily uneconomical and, beyond a certain number of Φ_0^k which depends on the state under consideration, convergence is elusive. On the other hand, according to the SST the correlation correction beyond a compact Φ_0 can be picked up efficiently, for ground as well as for excited states, in terms of separately chosen and variationally optimized analytic virtual orbitals. This fact is known from our calculations of electronic structures in $O(3)$ symmetry (atoms). Here we shall give an example of a similar result for electronic structures in $D_{\infty h}$ symmetry.

B. Electron correlation beyond the Fermi-sea Φ_0

1. Computation of the Φ_n

The most general method of obtaining electron correlation beyond Φ_0 is the diagonalization of the Hamiltonian matrix constructed from the wave function (1) in its trial form. The construction of this matrix requires the explicit form of Φ_n . These represent single, pair, pair-pair, etc., excitations from occupied numerical molecular or-

bitals (MO) in Φ_0 to virtual MO's (VO's) in Φ_n . For each VO, all possible symmetry-adapted configurations are constructed. These are determined by using Shaefer's quantum chemistry program exchange (QCPE) direct diagonalization program HEDIAG [14] (see Appendix). Having constructed the Φ_n , the energy matrix is diagonalized, either in small parts for each correlation function or fully for each value of the set of parameters characterizing the VO's. The parameters are varied so that the final solution corresponds to the energy minimum.

2. Choice and optimization of the virtual orbitals

In order to construct the virtual orbitals entering in Φ_n we consider three possibilities. The first is to extend the MCHF calculation of Φ_0 by including a few more configurations from the set of Φ_n . The second is to use elliptical basis functions [15]

$$\psi(\mathbf{r}) = e^{-\alpha\xi\xi\beta(\xi^2-1)^{m/2}} e^{-\gamma\eta\eta\delta(1-\eta^2)^{m/2}} e^{im\varphi}. \quad (4)$$

These are four-parameter function ($\alpha, \beta, \gamma, \delta$) of the form

$$\Xi_{\alpha,\beta}(\xi) H_{\gamma,\delta}(\eta) e^{im\varphi} \quad (5)$$

and must also be expanded in partial waves in the same manner as the OEDO's [Eq. (2)]. In principle, each virtual orbital is to be variationally optimized with respect to the nonlinear parameters ($\alpha, \beta, \gamma, \delta$). By expanding the terms of the form $(\xi+1)^q$ or $(1\pm\eta)^j$ in the OEDO functions [Eqs. (A4) and (A5)], we see that the OEDO's are essentially sums of elliptic basis functions, since the singular behavior is common to both.

This leads to the third possibility of VO's which we found to be very efficient and practical. We use parametric OEDO's as VO's. Then the description of the VO is more natural to the diatomic molecule, whereby the nonlinear variational parameters are reduced to two, e.g., the effective nuclear charges. This procedure is much faster than the individual four-dimensional optimization and has yielded satisfactory results. Moreover, it gives some intuition as to what kind of orbitals the electrons would "like" to be excited to. These VO's in OEDO form are directly comparable to the Sturmian-like functions, used as virtual orbitals in atomic calculations. They both share the characteristic that their effective nuclear charge is large enough to contract the otherwise diffuse virtual orbital, so as to describe an electron at positions comparable to the occupied orbitals, with the result that their energies become generally large and negative (see pp. 124–139 or Ref. [2] for choice and optimization of virtual orbitals).

The variational procedure may generally lead to local minima in the energy hypersurface. In order to reduce this danger and expedite convergence, the VO's must be properly initialized. If a VO is to describe an excitation from some MCHF molecular orbital to it, the electron should be located in the same space region as in the specific MO which is replaced. Accordingly, the VO's parameters are initially chosen so that the expectation value of some operator related to the electronic position be the same, for example $\langle \text{MO} | \xi^\lambda | \text{MO} \rangle = \langle \text{VO} | \xi^\lambda | \text{VO} \rangle$,

where $\lambda=1$ or -1 , or the overlap $\langle \text{MO} | \text{VO} \rangle$ be maximum. It turns out that initialization by overlap is sufficient.

Each VO is then made orthogonal to all lower-lying orbitals, either MCHF or virtual, and the nonlinear parameters are varied so as to eventually minimize the energy. This procedure determines variationally optimal parameters for each VO.

IV. APPLICATION TO THE SHORTEST BOND KNOWN: THE $\text{He}_2^{2+} \ ^1\Sigma_g^+$ GROUND STATE

A. Essential background

As regards the question of limits of efficiency and accuracy, small systems are the commonly accepted prototypes. The $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state was chosen since its wave function and potential-energy surface (PES) have unusual features, and since there exist accurate results from representative conventional methods for the computation of electron correlation [16–18].

The equilibrium distance of $\text{He}_2^{2+} \ ^1\Sigma_g^+$ constitutes the shortest bond known. It is computed to be [16–18] $R_e = 1.33$ a.u. Given that the charge distribution is compact, the calculation at equilibrium is very demanding if high accuracy is desired. Furthermore, the PES of He_2^{2+} has a volcanolike form (Fig. 1), where the minimum is local, lying above the energy of the dissociated products, $\text{He}^+ + \text{He}^+$. (This fact was first computed and interpreted by Pauling [19], in terms of the mixing of different ionic structures). Thus, apart from its minimum, it is characterized by the barrier and its maximum corre-

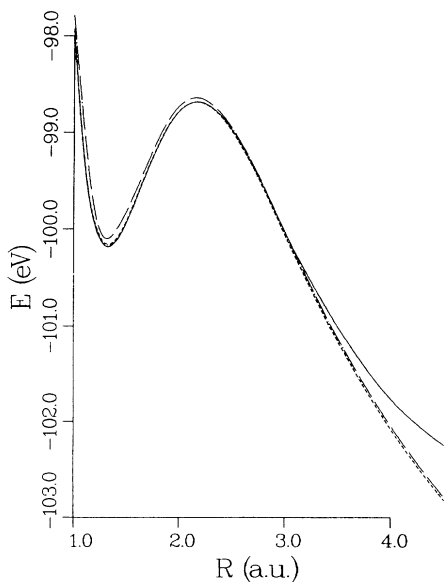


FIG. 1. Energy (in a.u.) vs nuclear separation (in a.u.) of the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state along with those of Refs. [16–18]. Solid line: Yagisawa, Sato, and Watanabe [16]. A dotted line and a dashed line represent the results of this work and of Valtazanos and Nicolaides [18], respectively. These two lines are indistinguishable in this scale. For details see Figs. 2(a)–(c). Dashed-dotted line: Metropoulos, Nicolaides, and Buenker [17].

TABLE I. The convergence of the SST scheme for the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state when Φ_0 consists of two configurations, $1\sigma_g^2$ and $1\sigma_u^2$, and four virtual orbitals are added sequentially, as shown in the first column. The second column shows the total number of configurations used to obtain the energy shown in the third column. $R = 1.4$ a.u.

Orbitals	Φ_n	Energy (a.u.)
Φ_0	2	−3.6636
Above $+2\sigma_g$	4	−3.6665
Above $+1\pi_u$	5	−3.6733
Above $+2\sigma_u$	7	−3.6739
Above $+3\sigma_g$	9	−3.6740

sponding to the transition state as well as by the $1/R$ repulsive form at large internuclear separation. The relative importance of the zeroth-order terms and of the correlation effects, describing covalent as well as ionic bonding, vary as we move across these three physically significant regions. Therefore, a good theory should yield consistently accurate results in all three of them.

The calculations of this work are variational and will be compared with three previous large scale variational calculations. The oldest one is by Yagisawa, Sato, and Watanabe [16] who employed the James-Coolidge method [20] in which the basis sets depend explicitly on r_{12} . The number of such basis functions was 75 and single-parameter optimization was carried out at each R . The other two calculations have been performed in this institute [17,18]. Both followed the conventional CI approach with large basis sets. The first [17] employed the extrapolation technique of the MRD-CI program [21] with a threshold of $10 \mu\text{H}$, thus improving convergence. We found that for $R > 3$ a.u. (i.e., beyond the barrier maximum), the conventional LCAO-CI yields lower results than those of Ref. [16]. The second computation [18] was

TABLE II. The convergence of the SST scheme for the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state when the MCHF Φ_n , beyond Φ_0 ($1\sigma_g^2, 1\sigma_u^2$), are six configurations ($2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_g^2, 2\pi_u^2$, and $3\sigma_u^2$) and 16 virtual orbitals are added sequentially. $R = 1.4$ a.u. The columns are described in Table I.

Orbitals	Φ_n	Energy (a.u.)
Φ_0	8	−3.677 15
Above $+1\pi_u$	11	−3.6774
Above $+1\delta_g$	12	−3.677 78
Above $+4\sigma_g$	16	−3.677 80
Above $+5\sigma_g$	21	−3.677 81
Above $+3\pi_u$	26	−3.6779
Above $+6\sigma_g$	32	−3.6780
Above $+2\pi_g$	35	−3.6781
Above $+4\sigma_u$	39	−3.678 15
Above $+1\delta_u$	40	−3.678 25
Above $+4\pi_u$	47	−3.678 41
Above $+2\delta_g$	50	−3.678 42
Above $+1\phi_u$	51	−3.678 45
Above $+7\sigma_g$	58	−3.678 50
Above $+5\sigma_u$	63	−3.678 51
Above $+3\pi_g$	68	−3.678 53
Above $+5\pi_u$	77	−3.678 55

a full CI using the MELDF programs [22]. A *very* large basis set was used [18] consisting of $15s$, $10p$, $4d$, and $1f$ functions, with exponents ranging from 43 000 to 0.008. These results are superior to the previous ones [17]. However, they are still higher than those of the James-Coolidge method in the range $R < 2.4$ a.u. (See Figs. 1 and 2.)

B. Results

In order to study the convergence of our scheme we performed three tests at $R = 1.40$ bohr, using different Φ_0 and Φ_n [Eq. (1)]. The results are shown on Tables I–III. In each case, Φ_0 is composed of the configurations $1\sigma_g^2$ and $1\sigma_u^2$, consisting of doubly occupied MCHF orbitals, and Φ_n are configurations describing possible excitations

from the Φ_0 orbitals to each VO (either MCHF or analytic). Tables I–III show Φ_0 along with the MCHF Φ_n , the virtual orbitals, the number of configurations used, and the corresponding energies.

(i) Φ_0 consists of $1\sigma_g^2$ and $1\sigma_u^2$, computed self-consistently. Four VO's have been added variationally, shown in Table I along with the corresponding energies. The MCHF energy is -3.664 a.u. With increasing virtual space the SST energy converges to -3.674 a.u.

(ii) Φ_0 as in (i) with six more Φ_n configurations has been computed within MCHF. Sixteen VO's have been added variationally. The MCHF energy is -3.6772 a.u. while the full SST energy is -3.6786 a.u. Details are shown in Table II.

(iii) Φ_0 as in (i) with 23 more Φ_n configurations that have been computed within MCHF, and 18 VO's have

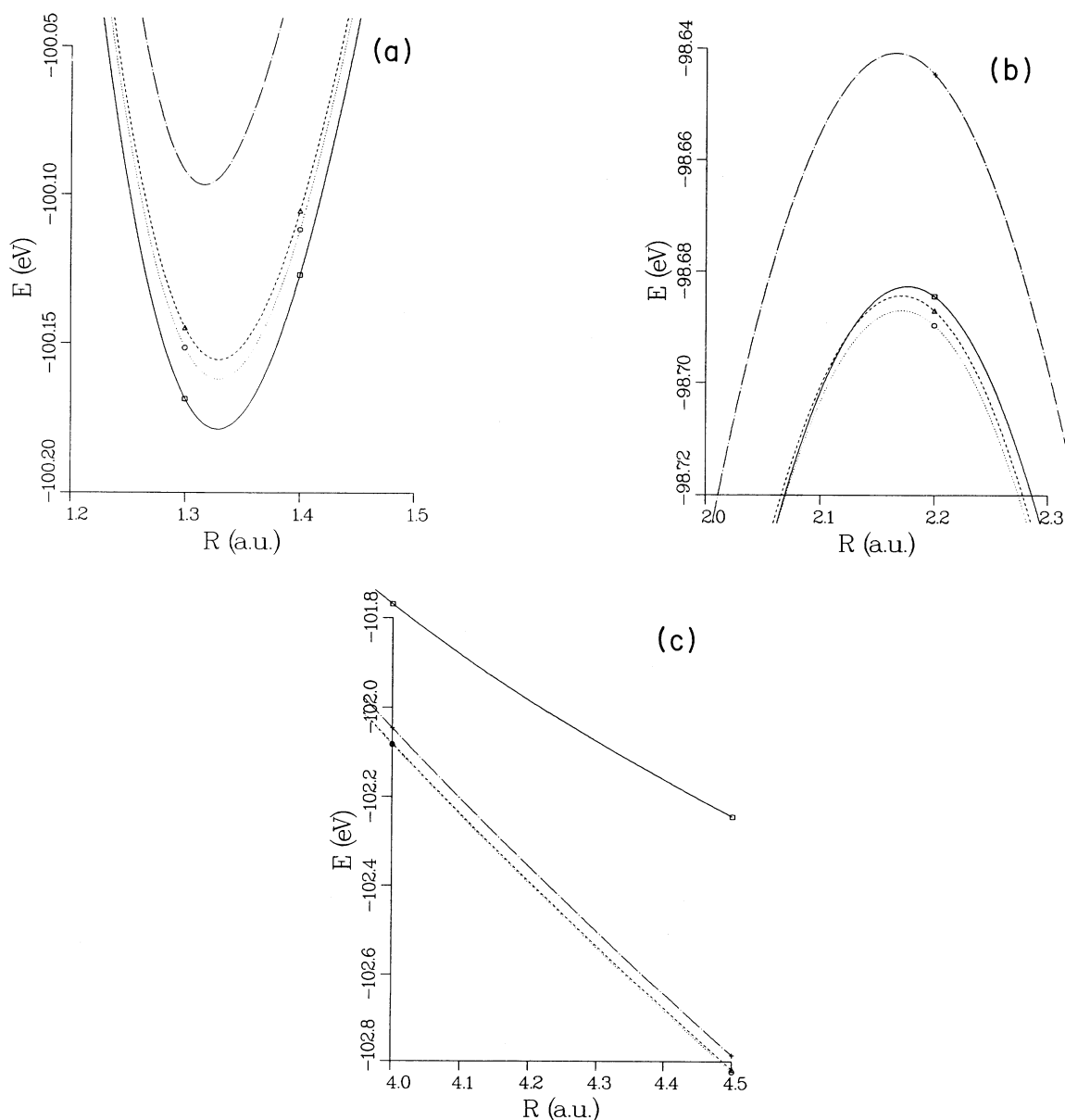


FIG. 2. (a) Same as Fig. 1 at the region of the minimum. (b) Same as Fig. 1 at the region of the maximum. (c) Same as Fig. 1 for nuclear separations $R > 4$ a.u.

TABLE III. The convergence of the SST scheme for the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ state when the MCHF Φ_n , beyond Φ_0 ($1\sigma_g^2, 1\sigma_u^2$), are 23 configurations ($2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_g^2, 2\pi_u^2, 3\sigma_u^2, 1\pi_u^2, 1\delta_g^2, 4\sigma_g^2, 5\sigma_u^2, 3\pi_u^2, 6\sigma_g^2, 2\pi_g^2, 4\sigma_u^2, 1\delta_u^2, 4\pi_u^2, 2\delta_g^2, 1\phi_u^2, 7\sigma_g^2, 5\sigma_u^2, 3\pi_g^2, 5\pi_u^2$, and $8\sigma_g^2$) and 18 virtual orbitals are added sequentially. $R = 1.4$ a.u. The columns are described in Table I.

Orbitals	Φ_n	Energy (a.u.)
Φ_0	25	-3.679 015
Above + $3\delta_g$	28	-3.679 022
Above + $6\sigma_u$	34	-3.679 024 6
Above + $6\pi_u$	40	-3.679 024 7
Above + $2\delta_u$	42	-3.679 043
Above + $2\phi_u$	44	-3.679 053
Above + $9\sigma_g$	53	-3.679 054
Above + $4\pi_g$	57	-3.679 061
Above + $4\delta_g$	61	-3.679 086
Above + $1\phi_g$	62	-3.679 097
Above + 9 more ^a	116	-3.679 10

^a $10\sigma_g, 7\sigma_u, 7\pi_u, 5\pi_g, 5\delta_g, 8\pi_u, 3\delta_u, 3\phi_u$, and $6\pi_g$, with 72, 79, 86, 91, 96, 104, 107, 110, and 116 configurations, respectively.

been added variationally, shown in Table III along with the corresponding configurations. The MCHF energy is -3.679 01 a.u. while the full SST energy is -3.679 10 a.u.

In general, when n in the virtual orbitals increases, the effective nuclear charges increase (in the He_2^{2+} case they may grow up to $Z^* \cong 25$) so that the average electronic position for the VO's with large quantum numbers be similar to that of the occupied orbitals. This also means that contributions from electronic positions closer to the

nuclei gradually become important, as the overall wave function tries to satisfy the cusp conditions.

The energies of the last calculation are shown in Table IV along with those of Yagisawa, Sato, and Watanabe [16], Metropoulos, Nicolaides, and Buenker [17], and Valtazanos and Nicolaides [18], and they are plotted in Fig. 1. Portions of Fig. 1 corresponding to the minimum of the curve, the maximum, and the large nuclear separations ($R \gtrsim 3$ a.u.) are shown in Figs. 2-4, respectively. The SST results, based on 43 orbitals and 116 configurations, are lower than those obtained by full CI [18], using 158 basis functions and 2282 configurations, or by extrapolated multiple-reference double-excitation configuration interaction and a smaller basis [17], by at least 10^{-4} a.u., for all nuclear separations. For $R \gtrsim 2$ a.u., which is just before the maximum, they are still lower than those of Yagisawa, Sato, and Watanabe [16] by even 10^{-2} a.u. They are only inferior around the minimum, (by 4×10^{-4} a.u.) where the bond is extremely short and relatively large contributions to electron correlation come from the region $r_{12} \rightarrow 0$.

V. CONCLUSIONS

The theory of this paper addresses the problem of the efficient and reliable computation of electronic structures of diatomics, in ground or in excited states. It starts with the form depicted by Eq. (1) and aims at the state-specific and optimal computation of Φ_0 and of Φ_n separately, thus avoiding the drawback of the conventional approaches which are based on the use of a common atomic orbital basis set [23].

TABLE IV. The potential-energy surface of the $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground state obtained by different theories. Column 1: Yagisawa, Sato, and Watanabe [16], obtained by the James-Coolidge method [20] with 75 basis functions optimized at each R . Column 2: our numerical MCHF calculation with Φ_0 and Φ_n as in Table III. Column 3: Valtazanos and Nicolaides [18] obtained by full CI [18], using 158 basis function and 2282 configurations. Column 4: Metropoulos, Nicolaides, and Buenker [17], obtained by the MRD-CI [21] method.

R (a.u.)	Ref. [16]	MCHF	Ref. [18]	Ref. [17]	$\Phi_0 + 18$ VO's ^a
1.0	-3.599 73	-3.598 97	-3.598 730 6	-3.5937	
1.1	-3.648 96	-3.648 25	-3.647 984 3		
1.2	-3.672 96	-3.672 29	-3.672 023 3	-3.6677	-3.672 38
1.3	-3.681 10	-3.680 47	-3.680 223 0		-3.680 56
1.4	-3.679 57	-3.679 01	-3.678 779 7	-3.6755	-3.679 10
1.5	-3.672 59	-3.672 08	-3.671 882 6		
1.6	-3.663 01	-3.662 58	-3.662 410 6	-3.6597	
1.7	-3.652 85	-3.652 50	-3.652 354 1		
1.8	-3.643 47	-3.643 20	-3.643 076 2	-3.6410	
1.9	-3.635 76	-3.635 58	-3.635 474 3		
2.0	-3.630 25	-3.630 18	-3.630 082 7	-3.6283	-3.630 25
2.2	-3.626 56	-3.626 75	-3.626 653 5	-3.6251	-3.626 79
2.4	-3.631 83	-3.632 30	-3.632 210 3	-3.6309	-3.632 33
2.5	-3.637 00	-3.637 69	-3.637 595 3		
3.0	-3.675 58	-3.676 90	-3.676 801 4	-3.6756	
3.5	-3.711 88	-3.717 54	-3.717 514 2	-3.7163	
4.0	-3.739 93	-3.751 44	-3.751 348 4	-3.7501	
4.5	-3.757 37	-3.778 69	-3.778 482 0	-3.7773	

^a $3\delta_g, 6\sigma_u, 6\pi_u, 2\delta_u, 2\phi_u, 9\sigma_g, 4\pi_g, 4\delta_g, 1\phi_g, 10\sigma_g, 7\sigma_u, 7\pi_u, 5\pi_g, 5\delta_g, 8\pi_u, 3\delta_u, 3\phi_u$, and $6\pi_g$. The correction is $O(10^{-5})$ and was calculated around the local extrema.

In its application to the demanding PES of the He_2^{2+} $^1\Sigma_g^+$ state (the PES contains a local minimum with the shortest known bond, a transition state and an ionically repulsive region), the herein new computational method has proven more efficient and accurate than the LCAO-based full-CI calculation with a huge basis set (158 functions) and overall more reliable than the r_{ij} -basis-dependent configuration interaction.

The major ingredients of this state-specific method are the following.

(i) The separation of Eq. (1) is adopted, where the diatomic orbitals of the multiconfigurational zeroth-order Φ_0 are obtained numerically. The advantage of such a calculation over the conventional LCAO-based one has been documented for atoms [1–4] and for diatomics (e.g., see the results of McCullough [24] and of Nicolaidis, Mercouris, and Piangos [25] on the hyperpolarizabilities of FH and of H^-). We argued that the expansion of the diatomic orbitals in partial waves has the advantage of treating not only diffuse ground states (e.g., negative ions [26]) but also Rydberg and doubly excited states with state-specific accuracy. By counting the nodes of the first partial wave, and hence identifying the desired orbital structure, convergence to the correct and radially optimized zeroth-order description is achievable.

(ii) The interelectronic correlations beyond the Fermi sea Φ_0 are incorporated in the Φ_n [Eq. (1)], which are symmetry-adapted configurations with one-, two-, etc. diatomic virtual orbitals whose parameters are optimized variationally by minimizing the total energy. The great advantage of this feature is that once even a small Φ_0 has been computed, convergence is rapid and guaranteed. This is not the case when one attempts to obtain Φ_n via the MCSCF procedure over the entire PES.

(iii) The calculation of the MCHF function as well as of the correlation vectors Φ_n is facilitated considerably, and in some case literally made possible [27], by the way the input is chosen. For the MCHF calculations, the input orbitals are the exact OEDO's expressed in prolate spheroidal coordinates. For the Φ_n calculations, the parameters of the diatomic virtual orbitals are initialized so as to maximize overlap with the occupied ones in Φ_0 [1–3].

ACKNOWLEDGMENTS

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APPENDIX A: OEDO INPUT TO THE NUMERICAL HF PROGRAM

By separating the one-electron diatomic orbital

$$\psi(\mathbf{r}) = \Xi(\xi)H(\eta)e^{\pm im\varphi}, \quad m = 0, 1, 2 \quad (\text{A1})$$

in prolate spheroidal coordinates $\mathbf{r} = (\xi, \eta, \varphi)$, where

$$\begin{aligned} \xi &= (r_a + r_b)/R, \\ \eta &= (r_a - r_b)/R, \end{aligned} \quad (\text{A2})$$

φ is the azimuthal angle, the Schrödinger equation for a one-electron diatomic molecule is separated into [12]

$$\begin{aligned} \frac{d}{d\xi} \left[(\xi^2 - 1) \frac{d\Xi}{d\xi} \right] \\ + \left[-c - p^2(\xi^2 - 1) - \frac{m^2}{\xi^2 - 1} + R(Z_a + Z_b)\xi \right] \Xi(\xi) \\ = 0, \quad (\text{A3a}) \end{aligned}$$

$$\begin{aligned} \frac{d}{d\eta} \left[(1 - \eta^2) \frac{dH}{d\eta} \right] \\ + \left[c - p^2(1 - \eta^2) - \frac{m^2}{1 - \eta^2} - R(Z_a - Z_b)\eta \right] H(\eta) \\ = 0. \quad (\text{A3b}) \end{aligned}$$

Here c , p^2 , and m are the separation constants, related to the energy E by

$$E = -\frac{2p^2}{R^2} + \frac{Z_a Z_b}{R}. \quad (\text{A3c})$$

The solution $\Xi(\xi)H(\eta)e^{im\varphi}$ is achieved by expansion in the series [13]

$$\begin{aligned} \Xi(\xi) = \left[\frac{\xi - 1}{\xi + 1} \right]^{m/2} (\xi + 1)^{R(Z_a + Z_b)/2p - 1} e^{-p\xi} \\ \times \sum_{j=0}^{\infty} g_j \left[\frac{\xi - 1}{\xi + 1} \right]^j, \end{aligned} \quad (\text{A4})$$

homonuclear

$$H(\eta) = \sum_{\substack{j=m \\ \text{or } m+1}}^{\infty} f_j^H P_j^m(\eta), \quad (\text{A5a})$$

heteronuclear (small R),

$$H(\eta) = e^{\pm p\eta} \sum_{j=m}^{\infty} f_j^{\pm} P_j^m(\eta), \quad (\text{A5b})$$

heteronuclear (large R)

$$H(\eta) = (1 - \eta^2)^{m/2} e^{\pm p\eta} \sum_{j=0}^{\infty} f_j^{\pm} (1 \mp \eta)^j, \quad (\text{A5c})$$

where $P_j^m(\eta)$ are associated Legendre polynomials. These expansions, when substituted in (A3), lead to recurrence relations for coefficients f_j and g_j , of the form

$$\begin{aligned} \alpha_j g_{j-1} + \beta_j g_j + \gamma_j g_{j+1} = 0, \quad j = 0, 1, 2, \dots \\ g_{-1} = 0, \end{aligned} \quad (\text{A6})$$

where α_j , β_j , and γ_j depend on R , Z_a , Z_b , p , c , and m . Power [13] solves the set of these simultaneous equations directly for p and c by expanding them in continuous fractions, using the Newton-Raphson method.

We use the values of p and c and the relations between $\alpha_j, \beta_j, \gamma_j$ and $R, Z_a, Z_b, p, c,$ and m in order to compute the expansion coefficients f_j and g_j , and from these to calculate the OEDO's.

For $\Xi(\xi)$,

$$\begin{aligned}\alpha_j &= (j-1-\sigma)(j-1-\sigma-m), \\ \beta_j &= Rz - c + (m+1)(m+\sigma-2p) - 2j(j-\sigma+2p), \quad (\text{A7}) \\ \gamma_j &= (j+1)(j+1+m),\end{aligned}$$

where $Rz = R(Z_a + Z_b)$ and $\sigma = Rz/(2p) - m - 1$.

For $H(\eta)$ homonuclear,

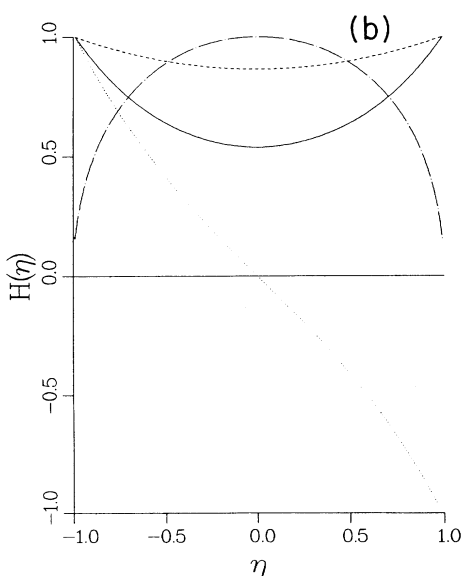
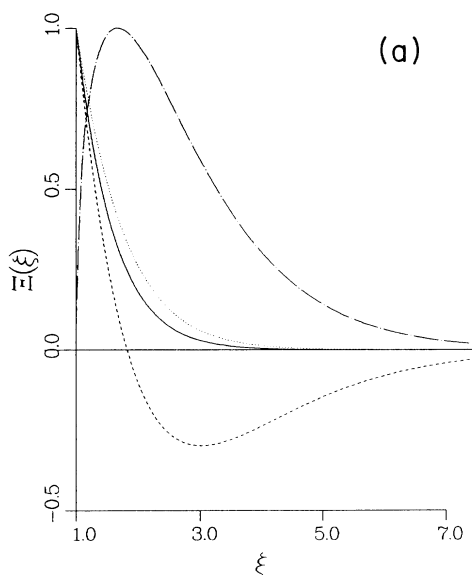


FIG. 3. (a) Input OEDO's along the ξ coordinate. Solid line: $1\sigma_g$. Dotted line: $1\sigma_u$. Dashed line: $2\sigma_g$. Dashed-dotted line: $1\pi_u$. The nuclear charges used are both 2, 2, 1.6, and 1.6, respectively. (b) Same as (a) but along the η coordinate.

$$\begin{aligned}\alpha_j &= p^2(j-1-m)(j-m)/[(2j-3)(2j-1)], \\ \beta_j &= c - j(j+1) + p^2 \left[\frac{(j+1-m)(j+1+m)}{(2j+1)(2j+3)} \right. \\ &\quad \left. + \frac{(j^2-m^2)}{(4j^2-1)} - 1 \right], \quad (\text{A8})\end{aligned}$$

$$\gamma_j = p^2(j+2+m)(j+1+m)/[(2j+3)(2j+5)],$$

heteronuclear (small R),

$$\begin{aligned}\alpha_j &= -\frac{j-m}{2j-1} [2pj + R(Z_a - Z_b)], \\ \beta_j &= c - j(j+1), \quad (\text{A8b})\end{aligned}$$

$$\gamma_j = \frac{j+1+m}{2j+3} [2p(j+1) - R(Z_a - Z_b)],$$

and (large R),

$$\begin{aligned}\alpha_j &= 2p(j+m) + R(Z_a - Z_b), \\ \beta_j &= c - j(j+1) - (m+2p)(2j+m+1) \\ &\quad - R(Z_a - Z_b), \quad (\text{A8c}) \\ \gamma_j &= 2(j+1)(j+1+m).\end{aligned}$$

We expand the OEDO's in partial waves over η . If

$$\Xi(\xi)H(\eta)e^{im\varphi} = \sum_{j=|m|}^{L_{\max}} X_j(\xi)Y_j^m(\eta,\varphi) \quad (\text{A9a})$$

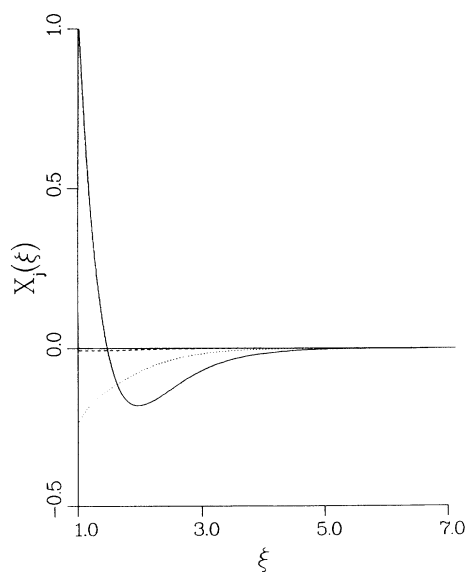


FIG. 4. The partial-wave functions (PW) $X_j(\xi)$, $j=1,2,3$ of $2\sigma_g$ treated as a MCHF virtual orbital at self-consistency. Solid line: $j=1$. Dotted line: $j=2$. Dashed line: $j=3$. We observe that the first PW $X_1(\xi)$ maintains the $2\sigma_g$ OEDO characteristics (shape, number of nodes, etc.).

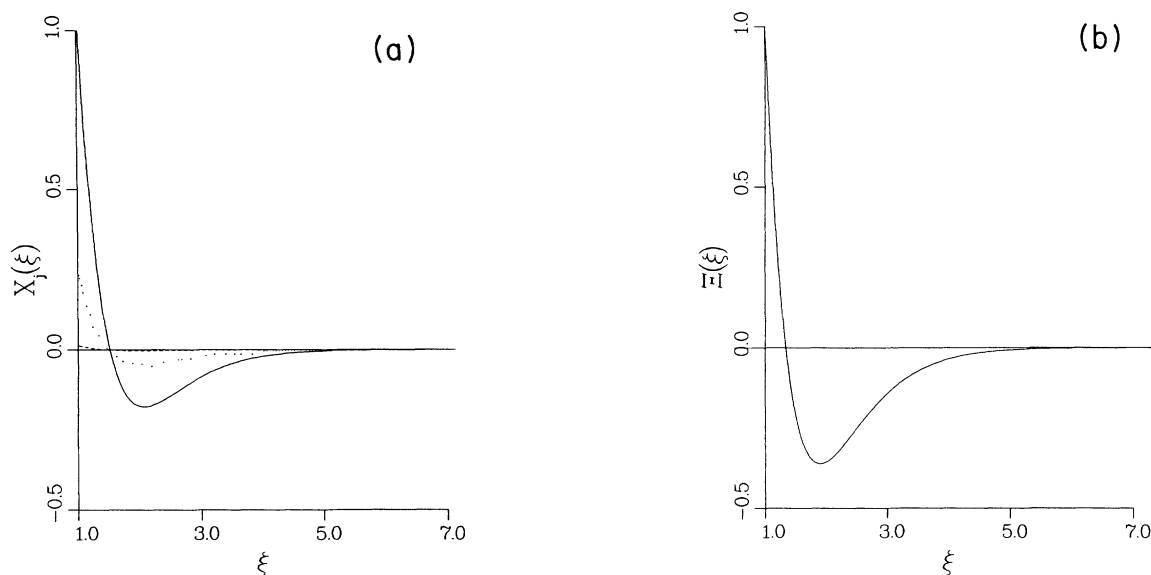


FIG. 5. (a) The partial-wave functions $X_j(\xi)$, $j=1,2,3$ of $2\sigma_g$ treated as OEDO VO after minimization of the energy and after orthogonalization with respect to the other orbitals $1\sigma_g$, $1\sigma_u$, and $1\pi_u$. Solid line: $j=1$. Dotted line: $j=2$. Dashed line: $j=3$. This orbital has not affected (and has not been affected by) the others. Its partial-wave functions are proportional to each other. (b) The $2\sigma_g$ OEDO VO after minimization of the energy, as input OEDO (before orthogonalization) along the ξ coordinate. The optimal effective nuclear charges are $Z_a^*=4.1$ and $Z_b^*=4.3$. We observe that the large nuclear charges contract the orbital in places comparable to those of the Fermi-sea orbitals ($\xi \lesssim 3$) in order to “facilitate” the electronic excitation.

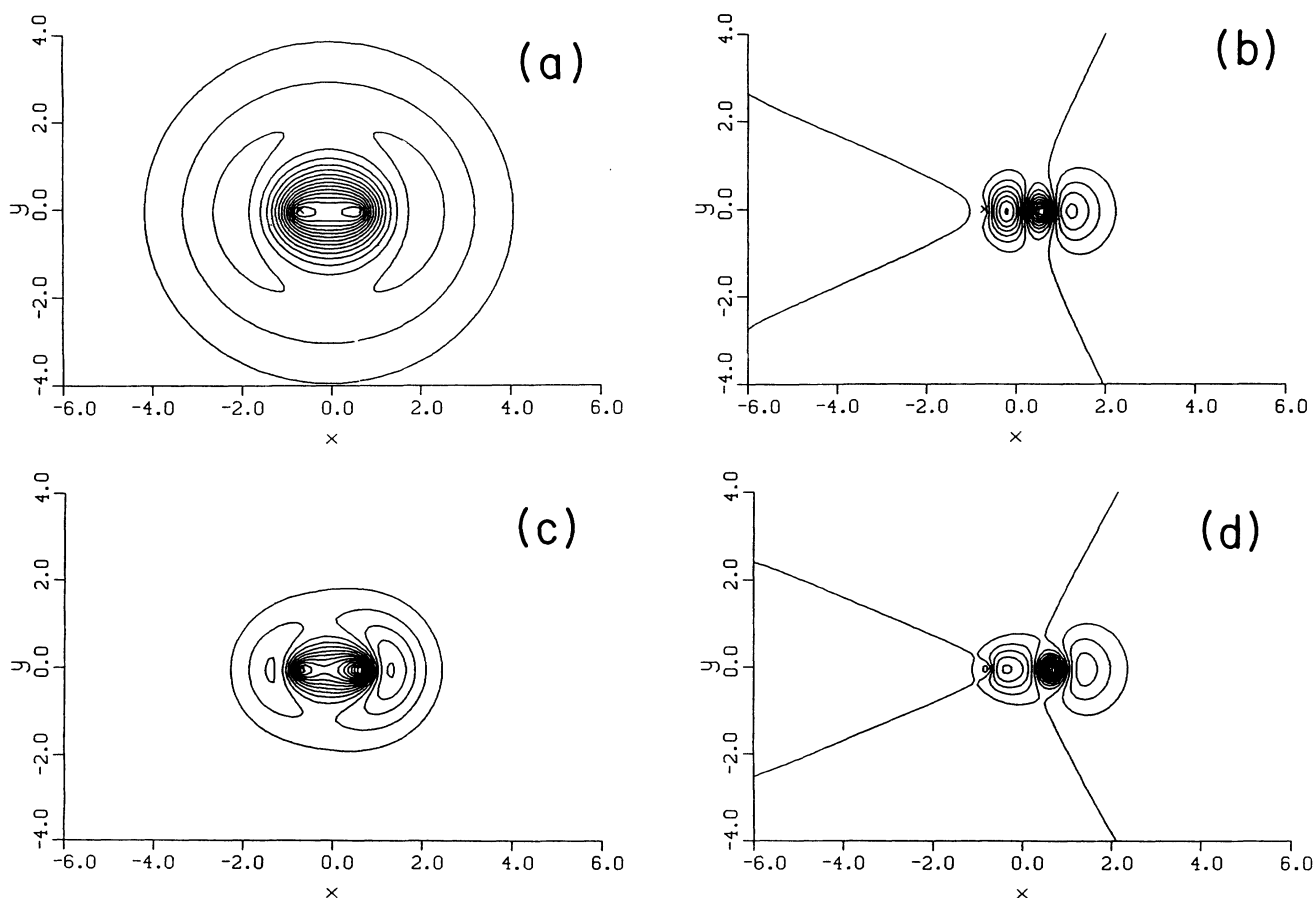


FIG. 6. Contour plot of the $2\sigma_g$ VO at $\varphi=0$. (a) OEDO input (before self-consistency). (b) MCHF VO after self-consistency. (c) Optimal VO input (minimizing the energy) before orthogonalization. (d) Optimal VO (minimizing the energy) after orthogonalization. The orthogonalization introduces new nodes making the OEDO VO similar to the MCHF VO (both after orthogonalization). The x axis is along the nuclei. The y axis defines the origin of the azimuthal φ angle.

and

$$H(\eta)e^{im\varphi} = \sum_{j=|m|}^{L_{\max}} a_j Y_j^m(\eta, \varphi), \quad (\text{A9b})$$

then

$$X_j(\xi) = a_j \Xi(\xi), \quad (\text{A9c})$$

where

$$a_j = \int Y_j^m(\eta, \varphi) H(\eta) e^{im\varphi} d\Omega. \quad (\text{A9d})$$

McCullough [11] treats $X_j(\xi)$ numerically for ξ large enough. For ξ close to 1 he expands them in power series over $\zeta = (\xi - 1)/2$, for $1 < \xi < \xi_0$,

$$X_j(\xi) = \zeta^{m/2} \sum_{k=0}^5 x_{jk} \zeta^k. \quad (\text{A10})$$

Accordingly, we expand $\Xi(\xi)$ in a similar power series for ξ close to $\xi = 1$,

$$\Xi(\xi) = \zeta^{m/2} \sum_{k=0}^5 x_k \zeta^k. \quad (\text{A11})$$

Then the expansion coefficients x_k obey the recurrence relations

$$\alpha_k x_k + \beta_{k-1} x_{k-1} + \gamma_{k-2} x_{k-2} = 2[4p^2 - R(Z_a + Z_b)]x_{k-3} + 4p^2 x_{k-4}, \quad (\text{A12})$$

where, in terms of R , Z_a , Z_b , p , c , and m ,

$$\alpha_k = \left[k + \frac{m}{2} \right]^2 - \frac{m^2}{4},$$

$$\beta_k = \left[k + \frac{m}{2} \right] (2k + m + 1) - c + R(Z_a + Z_b), \quad (\text{A13})$$

$$\gamma_k = \left[k + \frac{m}{2} \right] \left[k + \frac{m}{2} + 1 \right] - c - 4p^2 + 3R(Z_a + Z_b).$$

We match the analytic and the numerical expressions at ξ_0 .

APPENDIX B: CONFIGURATION INPUT TO THE NUMERICAL HF PROGRAM

The symmetry-adapted configurations are determined by using Shaefer's method (the QCPE program HEDIAG)

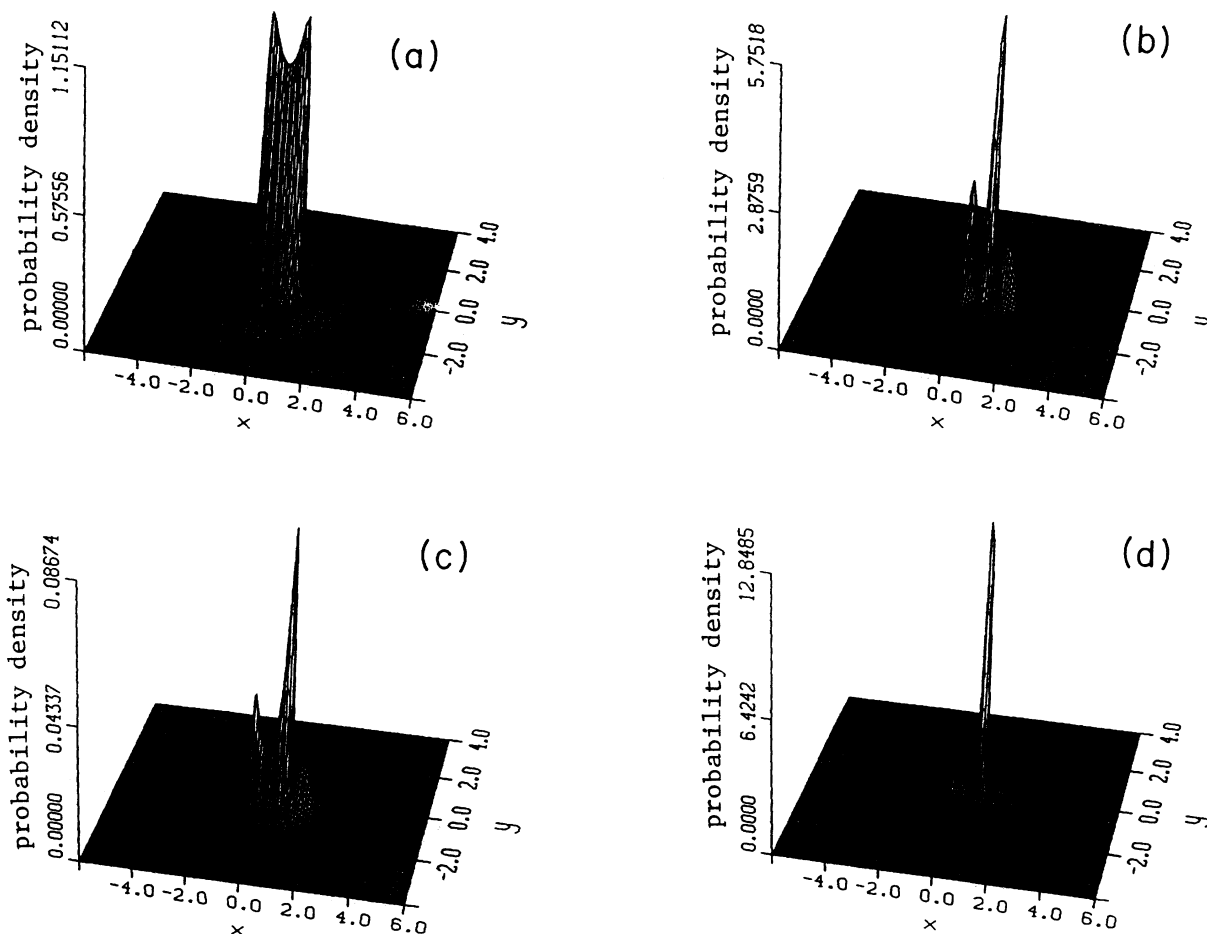


FIG. 7. The probability density for the $2\sigma_g$ VO along an arbitrary plane containing the nuclei. The labels (a)–(d) (and the comments) are as in Fig. 6.

[14], according to which those Slater determinants are chosen, which have the correct total m_s and m , and diagonalize the operator

$$(S^2 - \frac{1}{2}\chi_{\sigma_v}\sigma_v) \quad (\text{B1})$$

with the minimum eigenvalue [14]. Here S is the total spin and χ_{σ_v} is the character of the σ_v symmetry in the group $C_{\infty v}$.

APPENDIX C: NODES OF OEDO'S AND OF PARTIAL-WAVE FUNCTIONS

In this section we give examples and illustrations concerning the shape of the OEDO input orbital and of the partial-wave functions of the MCHF orbitals, as well as of the VO's in OEDO form, in the case of $\text{He}_2^{2+} \ ^1\Sigma_g^+$. Figures 3(a) and 3(b) show the OEDO functions $\Xi(\xi)$ and

$H(\eta)$, respectively, for the orbitals $1\sigma_g$, $1\sigma_u$, $1\pi_u$, and $2\sigma_g$. At self-consistency, the partial waves of these orbitals show almost the same shape, as in Fig. 3 except for the $2\sigma_g$. The partial-wave functions, $X_j(\xi)$, $j=1, \dots, 3$ of $2\sigma_g$ are shown in Fig. 4. We observe that the number of nodes of partial waves higher than first order is not conserved. However, the first one, $X_1(\xi)$, is very similar to the corresponding OEDO. This can be used for the identification of the $2\sigma_g$ orbital. The same orbital is shown in Fig. 5 as a VO in OEDO form within the SST treatment. The variational effective nuclear charges after the energy minimization are $Z_a^*=4.1$, $Z_b^*=4.3$. The contour plots of this orbital as OEDM input, MCHF, and VO are shown in Figs. 6(a)–6(d), respectively. Finally, Figs. 7(a)–7(d) show the probability density for an electron to be in this orbital, mapped on the zx plane (it is cylindrically symmetric along the z axis).

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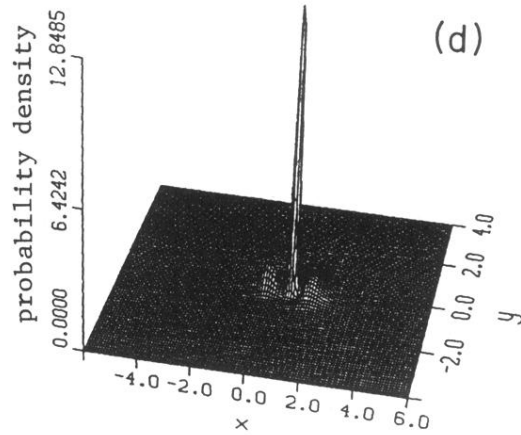
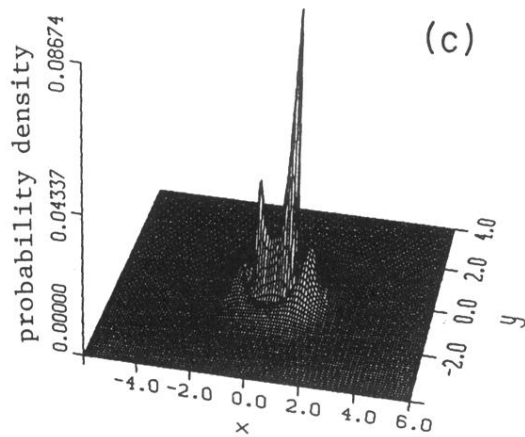
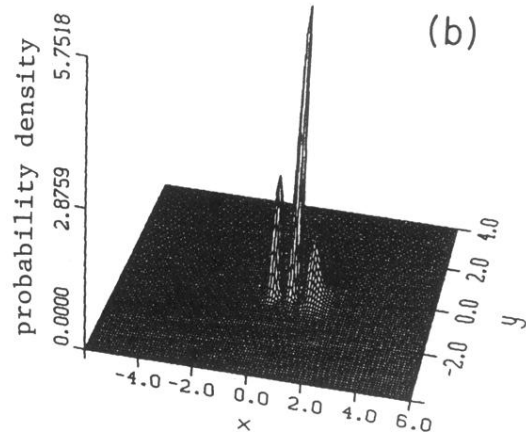
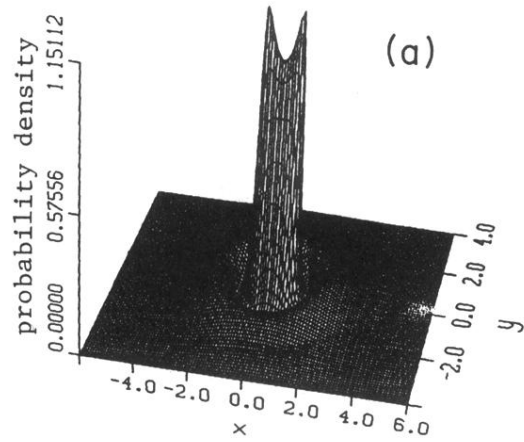


FIG. 7. The probability density for the $2\sigma_g$ VO along an arbitrary plane containing the nuclei. The labels (a)–(d) (and the comments) are as in Fig. 6.