An approximate frozen core approach to valence only molecular calculations*

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A simple valence electron-only theory based on an approximate frozen core approach and an exact core-valence strong orthogonality condition is developed for atomic and molecular systems. A unique reduced basis is introduced in which both core and valence orbitals are expanded. The core representation is roughly approximated, and the valence orbital overlap with the corresponding all-electron reference functions is nearly exact. The size of the reduced basis in terms of primitive functions is practically the same as that adopted by effective core potential methods in which the valence orbitals have the correct nodal properties. Results obtained with the present approach are presented for LiO, BeO and CaO molecules, and compared with the corresponding all-electron frozen core calculations. In addition, a detailed investigation on $Li_n Be$ clusters $(n = 1, \ldots, 6)$ is carried out.

Key words: Frozen core — Valence electron only — Reduced basis

1. Introduction

In this paper our previously proposed valence electron only (VEO) method [1] for the determination of the valence wavefunction is improved in some aspects and extended to open-shell systems. Valence electron methods are aimed at reproducing all-electron (AE) results without appreciable loss of accuracy, when the same kind of wavefunction and valence basis is used. The methods so far proposed may be classified into three main groups: the effective core potential

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

(ECP) methods [2–5], the methods based on the partitioning of the atomic volumes into core and valence regions [6] and, finally, the methods based on the frozen core approximation [7]. The present method belongs to this last group and may be characterized shortly as an *ab initio* reduced basis frozen core approach.

As shown in [7] the frozen core approach offers the advantage of preventing basis set superposition error when the innermost core orbitals are expanded in a relatively small basis of primitive functions. The atomic core orbitals usually employed in standard frozen core calculations are determined by optimizing the total atomic energy. However, when the interest is focused on studying valence electron wavefunctions, the use of energy optimized core orbitals is not particularly convenient; in fact, the core orbitals are just required to yield an effective Coulomb-exchange potential for the valence electrons. The basic idea underlying our procedure comes from the observation that the core–valence potential and the core–valence orthogonality constraints, characteristic of a good quality reference atomic basis set, can be approximated with high accuracy using a relatively small number of primitive functions for an "effective" description of the core orbitals. Obviously, the reduced basis is inadequate to give an accurate core electron energy. Its optimization is carried out with the aim of reproducing the shapes (including all the nodal properties) and the one-electron energies of the valence orbitals, expanded in a chosen reference basis set. This allows one to deal with valence orbitals of good quality, while the number of primitive functions necessary for the description of the core orbitals is smaller than that used in standard frozen core calculations.

The formalism is based on the separability theory [8] applied to many-electron systems in which strong orthogonality among wavefunctions of distinct subsystems (namely core and valence electrons) is assumed when evaluating the total energy. From this basic assumption the form of the one-electron effective hamiltonian arises in a natural way (Sect. 2). Details on the maximum overlap procedure adopted in the determination of the reduced atomic basis are given in Appendix 1. Appendix 2 contains the description of the direct energy minimization procedure devised for many-shell systems with frozen core orbitals.

Atomic results obtained from the optimization of the reduced basis sets for LI, Be, O and Ca atoms are presented together with test calculations on LiO, BeO and CaO molecules. The electronic structure of small $Li_n Be$ clusters is analysed and the reliability of the present computational approach in predicting minimum geometries, stabilities and ionization potentials is discussed on the basis of comparisons with the corresponding results of an AE treatment.

2. Outline of the method

Consider a molecular system built up by N atoms with individual core regions CI $(I = 1, \ldots, N)$, each containing N_{CI} electrons. The valence region of the whole molecular system contains N_v electrons which are supposed to give the most important bonding features. In this context, assuming that the total electronic

wavefunction may be expressed as a generalized product of functions in which the various group functions (i.e. the Slater determinants φ_C and φ_v) satisfy the strong orthogonality conditions $\varphi_c^\dagger \varphi_v = 0$ († denotes complex conjugate). The total energy of the system can be expressed as [5]

$$E = \langle \varphi_v | H_v | \phi_v \rangle + \sum_I E_{CI} + \sum_{I>J} E_{CI,CJ},$$

where $E_{CI,CJ}$ is the core–core interaction and E_{CI} is the core energy. The effective hamiltonian H_v for the N_v valence electrons i, j $(i, j = 1, \ldots, N_v)$ is given by

$$H_v = \sum_i \left\{ -1/2\Delta_i^2 - \sum_I Z_I/r_{iI} + \sum_I \sum_k [2J_k^{CI}(i) - K_k^{CI}(i)] \right\} + \sum_{i>j} 1/r_{ij}$$

$$= \sum_i f_c(i) + \sum_{i>j} g(i, j).$$

The first term of the last expression includes the core–valence interaction energy, $\langle \varphi_v | \sum_i f_c(i) | \varphi_v \rangle$, and the second term includes the intravalence energy $\langle \varphi_v | \sum_{i,j} g(i, j) | \varphi_v \rangle$.

Working within the conventional frozen core approximation, the orthogonality conditions can easily be taken into account. However, the core-valence orthogonality generates a modified valence basis which contains contributions from all the core orbitals φ^{CI}. This represents a severe drawback since the evaluation of the valence electron energy requires all the integrals needed in standard AE calculations. The same considerations apply to all the VEO procedures which explicitly adopt projection operators which are built with core orbitals expanded in a basis different from the one actually used for describing the valence states [3].

In order to overcome these difficulties it is convenient to define a reduced basis (that is a basis of relatively small dimensions) determined in such a way that the valence states computed with a reference AE basis are almost exactly reproduced, while the corresponding core states are approximated to a chosen degree of accuracy. The use of the reduced basis has two important consequences: the nodal properties of the reference valence AE orbitals are nearly exactly reproduced and, as the reduced basis dimension increases, the results become identical to those of frozen core calculations carried out with the AE reference basis set.

In the following, the procedure adopted in determining the reduced basis is briefly discussed. A given reference Gaussian basis set μ of dimension n_0 is used to expand the atomic orbitals φ which, following chemical intuition, may be classified as core orbitals φ_j^C $(j = 1, \ldots, m_C)$ and valence orbitals φ_k^v $(k = 1, \ldots m_v)$. Correspondingly, the basis functions μ can be partitioned into two subsets $\mu = (\mu^C, \mu^v)$, where the functions μ^C contribute most to the expansion of the core orbitals and similarly μ^v to the expansion of the valence orbitals.

Now we introduce a new atomic reduced basis set χ

$$\chi = (\chi_1 \chi_2 \cdots \chi_{n_r})$$

of dimension n_r smaller than that of the reference basis. The atomic core φ^C and valence φ^v orbitals are approximated by expanding them in terms of χ. Since

the reduced basis must be able to describe the valence orbitals with high accuracy, it is natural to assume that this basis is formed by the μ^v functions plus some tighter functions. The purpose of the tighter functions is to provide both an optimum description of the nodal properties of the valence orbitals and an effective core potential by roughly approximating the core orbitals. Starting with the reference orbitals $\varphi = (\varphi^C \varphi^v) = \mu T$, the new orbitals $\bar{\varphi} = (\bar{\varphi}^C \bar{\varphi}^v) = \chi V$ are determined by computing the expansion coefficients V according to a maximum overlap criterion as described in Appendix 1A. To improve the description of the valence orbitals $\bar{\varphi}_v$, some of the exponents α_χ are optimized at SCF level by minimizing the functional

$$Z(\alpha_\chi) = \sum_i [\,|\langle \bar{\varphi}_i^v | \varphi_i^v \rangle - 1| + |\bar{\varepsilon}_i - \varepsilon_i|\,].$$

Obviously, this procedure also affects the shape of the core orbitals $\bar{\varphi}^C$ which provide the effective Coulomb-exchange potential.

In molecular calculations the atomic basis is usually employed in a contracted form, with coefficients taken equal to the expansion coefficients of the SCF atomic orbitals. In the present approach, n_c contracted atomic orbitals are defined as

$$\varphi' = \lambda V' = \chi C W.$$

and the coefficient V' are determined according to the maximum overlap criterion (Appendix 1B).

The core–valence orthogonality, which is automatically satisfied in atomic systems, must also be satisfied and preserved in molecular systems when the optimization of the valence electron energy is performed. To this aim, after the basis set of atomic orthogonal orbitals $\bar{\varphi}(\chi)$ or $\varphi'(\lambda)$, denoted simply by $\varphi = (\varphi^C \varphi^v)$, has been expanded in a basis σ (χ or λ) of dimension $n(n_r$ or $n_c)$:

$$\varphi = (\varphi^C \varphi^v) = \sigma V = \sigma(V^C V^v).$$

the following steps are carried out.

1. When non-negligible core–core overlap between different centers occurs, the core orbitals φ^C must be orthogonalized according to

$$\hat{\varphi}^C = \varphi^C S_C^{-1/2} \quad \text{where} \quad S_C = V^{C\dagger} \sigma^\dagger \sigma V^c.$$

2. The projector $P^C = \hat{\varphi}^C \hat{\varphi}^{C\dagger}$ is used to generate the valence basis orthogonalized with respect to the core:

$$\bar{\varphi}^v = (I_n - P^C) \sigma V^v = \sigma Q.$$

with overlap matrix (of order n_v) $S_v = Q^\dagger \sigma^\dagger \sigma Q$.

3. S_v is used to obtain the valence orthogonal basis

$$\varphi^v = \sigma T.$$

by means of the Schmidt method.

In order to avoid a cumbersome two-electron integral transformation from the basis σ to the basis φ^v, it is preferable to work in the full σ space of dimension n which includes m_C redundancies due to the $\varphi^{C\dagger} \varphi^v = 0$ constraints. This requires only a simple transformation of the Fock matrices.

4. The orbital variation leading to the minimization of the valence electron energy is accomplished by an orthogonal transformation U (of order n_v) of the type

$$\bar{T} = TU, \quad \text{with} \quad \tilde{U}U = U\tilde{U} = I_{n_v}.$$

which maintains the orthogonality of the orbitals φ^v among themselves and against the core orbitals φ^C (see Appendix 2).

3. Preparation of atomic reduced basis

In our previous paper [1] the reduced basis have been determined for Li, Na, K and Cu atoms and tested in molecular calculations on the Li_2, Na_2, K_2 and CuH systems. In the present work the reduced basis is computed for Be, in order to study mixed Li_nBe clusters, and also for Ca and O atoms, in order to compare our results on LiO, BeO and CaO with those recently obtained by other VEO methods based on the ECP approach [4, 5].

For first row atoms, the reference AE basis (9/5) have been taken from [9], while for Ca the basis (14/9) of [10] has been augmented by two diffuse p functions [10] acting as polarization functions in the molecular calculations.

The results concerning the electronic ground states of the considered atoms are reported in Table 1 [11], where comparison is presented with the AE results. Both orbital energies and orbital shapes (as shown by the overlap integral value) of the reference AE valence states are reproduced with high accuracy. This indicates that the approximate representation of the core states in the reduced basis is sufficiently accurate to mimic the core-valence Coulomb and exchange potentials and also the core-valence orthogonality. The saving in computational time which can be achieved is estimated by considering that, for instance, for atoms K-Cu the number of primitive functions is 47 in the AE reference basis [10] and 26 in the optimized reduced basis. The actual dimension of the reduced basis is nearly one half of the reference AE one for the angular symmetries which include both core and valence states. In addition, the dimension of the reduced basis is close to that of the ECP approaches in which the pseudo-valence orbitals have the correct nodal properties [4, 5].

4. Molecular calculations

4.1. Oxides

In Table 2 our results on LiO, BeO and CaO are compared with frozen core calculations carried out with the AE reference basis and with recent ECP studies [4, 5]. The present SCF calculations have been performed using the basis of Table 1 with the following contraction schemes: (311/11) and (311/2) for Li and Be; (311/32) and (22211/2211) for O and Ca atoms, respectively. The results concerning equilibrium bond distances, harmonic frequencies, dipole moments and dissociation energy compare well with those obtained with a full reference basis and by ECP calculations [4, 5]. This confirms the reliability of the reduced basis approach for highly ionic molecules, as well as for covalent molecules.

Table 1. Optimized reduced basis sets for Li, Be, O and Ca atoms[a]

	Exponents	Contraction coefficients		Exponents	Contraction coefficients
$Li(^2S)$					
s	27.05303	0.095502	p	0.24592	0.511531
	3.96364	0.503636		0.06237	0.612820
	0.78325	0.554430			
	0.07170	1.000000			
	0.02876	1.000000			
	$\varepsilon(2s) = -0.1955\ (-0.1963)$			$\langle \varphi^{AE} \vert \varphi \rangle = 0.99996$	
$Be\ (^1S)$					
s	43.34113	0.117000	p	0.50816	0.511531
	6.73201	0.490153		0.12888	0.612820
	1.59634	0.535372			
	0.17279	1.000000			
	0.05861	1.000000			
	$\varepsilon(2s) = -0.3079\ (-0.3077)$			$\langle \varphi^{AE} \vert \cdot \varphi \rangle = 0.99997$	
$O\ (^3P)$					
s	243.47194	0.082714	p	11.67587	0.143412
	39.96437	0.381035		5.93620	0.150702
	9.39382	0.660253		2.15297	0.799647
	0.92218	1.000000		0.69151	0.651214
	0.28772	1.000000		0.20730	0.445177
	$\varepsilon(2s) = -1.2418\ (-1.2418)$			$\langle \varphi^{AE} \vert \varphi \rangle = 0.99997$	
	$\varepsilon(2p) = -0.6288\ (-0.6290)$			$\langle \varphi^{AE} \vert \varphi \rangle = 0.99995$	
$Ca\ (^1S)$					
s	550.21923	0.264275	p	14.67977	0.720214
	83.79586	0.828312		4.90273	0.353796
	7.90510	0.457825		0.78469	0.911838
	3.97775	0.563383		0.30900	0.111297
	0.97706	0.484274		0.11247	1.000000
	0.39615	0.551810		0.04039	1.000000
	0.06594	1.000000			
	0.02690	1.000000			
	$\varepsilon(4s) = 0.1955\ (-0.1955)$			$\langle \varphi^{AE} \vert \varphi \rangle = 1.00000$	

[a] In parenthesis the orbital energies of the AE reference basis are reported. $\langle \varphi^{AE} \vert \varphi \rangle$ is the overlap integral between reference AE and reduced basis valence orbitals

4.2. Mixed Li_nBe clusters

In recent years, the electronic structure of small alkali and alkaline-earth metal clusters has been the object of intense theoretical study at different levels of approximation [12]. The study of mixed species, however, is almost completely lacking; the only examples are the HF-CI studies of Koutecky and Pewestorf [13] on Li_nBe systems and that of Bauschlicher et al. on small alkali-transition metal clusters [14].

The Li_nBe clusters have been considered in the present investigation in order to also check the reliability of our VEO procedure against the AE results on

Table 2. Molecular constants for LiO, BeO and CaO

	Reduced basis[a]		FC–AE[b]	ECP[c]
	A	B		
LiO ($^2\Pi$)				
r_e (a.u.)	3.258	3.205	3.190	3.224
μ_e (D)	6.77	6.66	6.60	7.37
ω_e (cm^{-1})	888	885	878	773
D_e (eV)	1.26	1.47	1.44	2.12
BeO ($^1\Sigma^+$)				
r_e (a.u.)	2.572	2.497	2.489	2.528
μ_e (D)	7.41	7.06	7.01	7.72
ω_e (cm^{-1})	1510	1721	1707	1544
D_e (eV)	0.51	1.01	0.92	3.37
CaO ($^1\Sigma^+$)				
r_e (a.u.)	4.444		4.375	5.032
μ_e (D)	4.28		4.25	
ω_e (cm^{-1})	311		334	281
D_e (eV)	−2.59		−2.59	−2.74

[a] Basis A: (311/2) for Li and Be, (22211/2211) for Ca; Basis B: (311/11) for Li and Be (see text)
[b] Results from frozen core calculations using the AE reference basis. (711/11) for Li and Be, (711/32) for O and (82211/6311) for Ca (see text)
[c] The ECP results for LiO and BeO are taken from [4], the D_e values a from CAS–SCF calculations. The ECP results for CaO are taken from [5]

systems characterized by unusual chemical bonds. The basis sets adopted for Li and Be atoms are those of Table 1 in a (311/2) contracted form. Such a basis set is only slightly lower in quality than that used in the AE study on Li$_n$Be clusters [13], and is of the same type as that used extensively for Li$_n$ clusters [15]. A geometry optimization with symmetry constraints has been performed for a few electronic states of neutral and positively charged Li$_n$Be clusters ($n \leqslant 6$, see chart on p. 400). Table 3 reports the results concerning the best geometry parameters, stabilities, and vertical and adiabatic ionization potentials. The stability of the neutral and ionic clusters has been evaluated according to $D_e = -E(\text{Li}_n\text{Be}) + (n-1)E(\text{Li}) + E(\text{Li}^{q+}) + (\text{Be}) \ (q = 0.1)$.

The best cluster geometries given by our SCF optimization can be rationalized by the following simple observations. The Be atom occupies a central position of a regular polyhedron, because in this way the number of the Be–Li bonds is maximum. All the distortions from the most symmetric configurations ($D_{\infty h}$, D_{3h} and T_d for Li$_2$Be, Li$_3$Be and Li$_4$Be, respectively) can be explained on the basis of Renner–Teller or Jahn–Teller effects [16]. These distortions, however, do not decrease the number of possible Be–Li bonds, with the exception of the Li$_3$Be system which is characterized by two Be–Li and two Li–Li bonds. In general, however, the cluster stability cannot be entirely ascribed to the Be–Li interaction: important Li–Li bonding does occur as shown by the fact that the mean Li–Li

$C_{\infty v}$ $C_{2v}, C_{\infty v}$ C_{2v}

T_d D_{4h} O_h
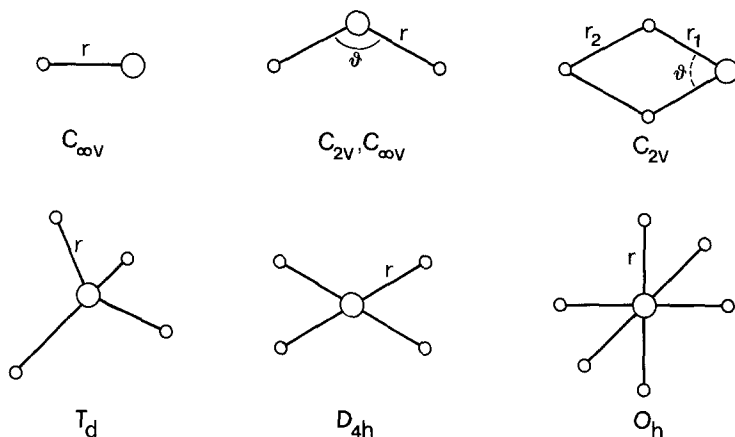
bond distance (about 6.5 a.u.) is still comparable with the nearest neighbour distance computed for Li_n clusters (5.7–6.2) a.u. [15].

As for the absolute value of the cluster stability, the present SCF results cannot be considered as conclusive, because, as is well known, the electron correlation effects can play a crucial role. However, on the basis of experience derived from studies on alkali metal clusters [15] the lack of correlation in our treatment probably has no great impact on the basic cluster structure which is usually predicted to a good approximation as SCF level.

From the analysis of the results of Table 3, one can note that the present computational method is able to reproduce in a fairly good manner the best geometries obtained by the AE treatment. The stability of the clusters is always slightly underestimated, even if the qualitative trend is correctly predicted. This is not a surprising result considering that the basis set used in the AE study [13] includes two p polarization functions on each atom. Possible core polarization effects, which can give non-negligible contributions to the cluster stability, can be incorporated into our approach according to the method proposed in [17].

5. Conclusions

The results of test calculations made on some oxides and $Li_n Be$ clusters show overall good performance of the proposed reduced basis approach. The method is capable of simulating very closely the AE frozen core reference calculations with reduced computational effort. The reduction in computational effort is due mainly to the sensible reduction of the number of primitive functions included in the basis set and to the remarkable simplicity and flexibility of the computational procedure. Particularly important is the point that the number of primitive functions of our reduced basis is practically equal to that used in ECP approaches [4, 5], and smaller than that of standard frozen core calculations employing energy optimized core orbitals. Some advantages offered by the reduced basis approach are: (i) valence orbitals come out in a direct way to be very close to the corresponding AE ones; (ii) there is no need for parameter determination in

Table 3. Results of reduced basis SCF calculations on $Li_n Be$ clusters[a]

Cluster	Geometry	E_v (a.u.)	D_e (eV)	IP (eV)[b]	
				Vert.	Adiab.
LiBe+ ($^1\Sigma^+$)	$r = 5.12$ (5.10)	−0.96102	0.52 (0.58)		
Li$_2$Be ($^3B_1$)	$r = 5.11$ (4.86) $\theta = 73.0$ (74.3)	−1.32321	0.01 (0.26)	4.20	3.97
Li$_2$Be+ ($^2A_1$)		−1.16789	0.96		
($^2B_1$)		−1.15593	0.64		
($^2A_1$)	$r = 7.60$ $\theta = 45.0$	−1.17650	1.20		
Li$_2$Be ($^1\Sigma_g^+$)	$r = 4.92$ (4.87) $\theta = 180.0$	−1.33133	0.23 (0.32)	3.67	3.66
Li$_2$Be+ ($^2\Sigma_g^+$)		−1.19662	1.74		
($^2\Sigma_g^+$)	$r = 4.96$ (5.00) $\theta = 180.0$	−1.19666	1.74 (1.83)		
Li$_3$Be ($^2B_2$)	$r_1 = 4.81$ (4.91) $r_2 = 6.11$ (5.98) $\theta = 80.0$	−1.52966	0.44 (0.72)	4.08	
Li$_3$Be+ ($^1A_1$)		−1.37960	1.54 (2.13)		
Li$_4$Be (T_d)(1^3T_1)	$r = 4.54$ (4.51)	−1.71431	0.28 (0.74)	2.67	2.66
(2^3T_1)	$r = 4.50$	−1.71292	0.24		
Li$_4$Be+ (T_d)($^4A_1$)		−1.61630	2.80		
($^2T_2$)		−1.57984	1.80		
($^2T_1$)		−1.57770	1.75		
($^4A_1$)	$r = 4.60$	−1.61666	2.81		
($^2T_1$)	$r = 4.56$	−1.58140	1.85		
($^2T_2$)	$r = 4.56$	−1.58050	1.82		
Li$_4$Be (D_{4h})($^1A_{1g}$)	$r = 4.75$ (4.69)	−1.74576	1.14 (1.25)	3.55	3.55
Li$_4$Be+ (D_{4h})(^2E_u)		−1.61527	2.77		
(^2E_u)	$r = 4.80$	−1.61534	2.77		
Li$_6$Be ($^1A_1$)	$r = 4.58$ (4.52)	−2.19233	2.92 (3.28)	3.60	3.60
Li$_6$Be+ ($^2T_{1u}$)		−2.06000	4.50		
($^2T_{1u}$)	$r = 4.61$	−2.06013	4.51		

[a] In parentheses the AE results of [13] are reported. See chart for the definition of the geometry parameters: bond distances in a.u., valence angles in degrees. When not given the geometry of the ionic form is the same as that of the corresponding neutral cluster
[b] IP vert. and IP adiab. mean vertical and adiabatic ionization potential, respectively

order to build the effective core operator and, therefore, no additional integrals are required; (iii) all the orthogonality constraints are exactly satisfied at every step of the calculation.

Appendix 1

A. Assuming the expansion coefficients, T, of the orthogonal set of functions $\varphi = (\varphi_1, \ldots, \varphi_{m_0})$, are known in terms of the reference basis set μ, i.e. $\varphi = \mu T$,

then the expansion coefficients V of the m_0 new functions, $\bar{\varphi} = (\bar{\varphi}_1, \ldots, \bar{\varphi}_{m_0})$, expressed in terms of the reduced basis set χ, i.e $\bar{\varphi} = \chi V$, are found by searching for the orthogonal matrix U_0 which maximizes the quantity

$$f(U_0, \alpha_\chi) = \text{tr}\,(\varphi^\dagger \bar{\varphi}_0 U_0).$$

Taking $U_0 = -I + 2P_0^{-1}$ (where $P_0 = I + X_0 - \tilde{X}_0$), the gradient with respect to the independent parameters X_0 is given by

$$f_x = 2P_0^{-1}(S_0 U_0 - \tilde{U}_0 \tilde{S}_0)\tilde{P}_0^{-1},$$

where $S_0 = \varphi^\dagger \bar{\varphi}_0 = \tilde{T}\mu^\dagger \chi V_0$ and the $\bar{\varphi}_0$ are some starting orbitals. The stationary conditions $f_x = 0$, i.e. $S_0 U_0 = \tilde{U}_0 \tilde{S}_0$, can be satisfied by finding the singular vectors Z_a and Z_b of S_0, such that

$$\tilde{Z}_a S_0 Z_b = \text{diagonal},$$

and taking $U_0 = Z_b \tilde{Z}_a$.

Then, from the initial guess V_0 the optimum coefficients $V = V_0 U_0$, i.e. the optimum orbitals $\bar{\varphi} = \bar{\varphi}_0 U_0$, are obtained. A natural simple choice is $V_0 = (\chi^\dagger \chi)^{-1/2}$.

B. A similar procedure has been followed to determine the best contraction coefficients. Let C be the $n_r \times n_c$ matrix defining the n_c contracted atomic functions λ according to $\lambda = \chi C$. The overlap matrix for the λ functions is $S_\lambda = C^\dagger \chi^\dagger \chi C$. The contracted atomic orbitals are defined as $\varphi' = \lambda V' = \chi C W$ (W is a $n_c \times m_0$ matrix), where both the C and W matrices are considered as independent variables, subjected, of course, to the conditions of orthonormality $\langle \varphi'_i | \varphi'_j \rangle = \delta_{ij}$ and normalization $(S_\lambda)_{ii} = 1$. Assuming as the initial guess the orthonormalized orbitals $\varphi'_c = \chi C S_\lambda^{-1/2}$, the new contracted orbitals $\bar{\varphi}'$ which have the maximum overlap with the $\bar{\varphi} = \chi V$ orbitals are expressed as $\bar{\varphi}' = \varphi'_c U_c$, where U_c is the orthogonal matrix of order n_c determined by finding the singular vectors Z_c and Z_d of the matrix $S_c = \varphi^\dagger \varphi_c = \tilde{V}\chi^\dagger \chi C S_\lambda^{-1/2}$. Partitioning the orthogonal matrix Z_d as $Z_d = (Z_d^0 Z_d^v)$, the matrix $U_c = (U_c^0 U_c^v)$ is given by $U_c^0 = Z_d^0 \tilde{Z}_c$ and $U_c^v = Z_d^v$.

Appendix 2

The valence electron energy can be written in general as

$$E_v = \langle \varphi_v | H_v | \varphi_v \rangle = \sum_i \nu_i \,\text{tr}\, \bar{R}_i f_c + \tfrac{1}{2}\sum_{i,j} \nu_i \nu_j \,\text{tr}\, \bar{R}_i G_{ij}(\bar{R}_j)$$

where the occupied valence orbitals are collected in n_s shells i, j $(=1, \ldots, n_s)$. The ith shell is formed by m_{0i} orbitals expressed as $\bar{T}_i^0 = TUI_i$ $(i = 1, \ldots, n_s)$. I_i is the diagonal matrix having m_{0i} diagonal elements equal to 1 at the right places to identify the orbitals belonging to the ith shell and zero elements elsewhere; ν_i is the shell occupation number (integer or fractional); $\bar{R}_i = \bar{T}_i^0 \, \tilde{\bar{T}}_i^0 = TUI_i^0 \tilde{U}\tilde{T}$ (where $I_i^0 = I_i \tilde{I}_i$) is the density matrix of the shell i. The definition of $G_{ij}(R_j)$ is standard and contains the coupling constants a_{ij} and b_{ij} which depend on the particular state under study.

As in our previous work, the orthogonal matrix U is taken as $U = -I_{n_v} + 2P^{-1}$, with $P = I_{n_v} + X - \tilde{X}$; the gradient G_x of E_v is computed with respect to the independent variables X. Introducing the definitions

$$h_i^0 = \tilde{T} h_i T. \quad \text{with} \quad h_i = \nu_i[f_c + \sum_j \nu_j G_{ij}(\bar{R}_j)].$$

and $D = \sum_i h_i^0 U I_i^0$ ($n_v \times m_0$), and assuming the orthogonal matrix U partitioned as $U = (U^0 U^v)$, the null gradient condition may be put into the form

$$U^0 \tilde{D} - D \tilde{U}^0 = 0.$$

The entire matrix U may be determined by the singular vectors of D: computing $\tilde{Z}_e D Z_f = $ a diagonal matrix and considering the partition $Z_e = (Z_e^0 Z_e^v)$ one has $U^0 = Z_e^0 \tilde{Z}_f$ and $U^v = Z_e^v$.

In order to ensure convergence, a simple level shifting procedure is devised by adding arbitrary negative constants, of common value d, say, to the diagonal elements of D; or, better, according to our experience, by modifying the matrix D_p at the cycle p as

$$D_p' = D_p - dU_{p-1}^0 \qquad (d > 0).$$

and computing U from the singular vectors of the modified matrix D_p'.

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