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Optimized virtual orbital space for high-level correlated calculations. II. Electric properties^{a)}

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The optimized virtual orbital space (OVOS) technique recently proposed for high-level correlated calculations of energy surfaces, is shown to be nearly as efficient for electric field properties. In particular, the polarizability of F⁻, and the dipole moment and polarizability of FH as a function of internuclear separation are studied. A reduction of the virtual space to about one-half has a negligible effect on the dipole moment and polarizabilities for FH and F⁻ examples. A further reduction to one-quarter is reliable when augmented with the exact second-order result, obtained as a by-product of the OVOS generation. This enables the extension of high-level correlated methods to systems at least 2–4 times larger than those that could be accurately studied using the full space of virtual orbitals.

I. INTRODUCTION

The overwhelming majority of advanced quantum mechanical calculations of the molecular electronic structure¹⁻³ are carried out today within the framework of the basis set concept. Computational experience shows that large and flexible basis sets have to be used in order to obtain sufficiently accurate theoretical predictions, but the basis set dimension is currently one of the major limiting factors in applications of modern methods of quantum chemistry¹⁻³ to chemical problems.

There are several ways of reducing the basis set size without considerably affecting the accuracy of the calculated molecular energies and other properties. One of them involves the optimization of basis set functions at either the atomic or molecular level. The recent proposal of generalized contractions by Almlöf and Taylor⁴ offers another attractive possibility. However, all those standard ways of circumventing the basis set dimensionality problem are still usually carried out at the atomic level. Hence, the resulting basis sets may not be flexible enough for multipurpose use in molecular calculations, or may be still too large to be used for polyatomic molecules of chemical interest.

A different approach to the reduction of the basis set size has recently been proposed by Adamowicz and Bartlett⁵ which might considerably extend the range of applications of high-level correlated methods of quantum chemistry. The idea of what is hereafter termed the optimized virtual orbital space (OVOS) method has originated from the observation that out of a very large set of available virtual orbitals resulting from SCF calculations for a sizable molecule only a relatively small number of them are highly efficient at the correlated level. The OVOS approach offers a systematic method of extracting the subspace of virtual orbitals of the given

dimension out of the full set of virtual orbitals with possibly minimal loss in the calculated correlation energies. The high efficiency of this method has been documented by different MBPT and CC calculations of molecular energies and their geometry dependence. Many other approaches for reducing the virtual space are summarized in Ref. 5 and references therein. In particular, density based (frozen) natural orbitals obtained from second order provide the initial approximation, from which subsequent iterations define the energy optimized OVOS.

An advantage of the OVOS method follows from the fact that the reduction of the virtual space dimension is performed at the molecular level. This allows the use of large and flexible atomic basis sets sufficient to describe several subtleties of the electron distribution in molecules. The reduction of the virtual orbital space at the molecular level should not considerably diminish the important aspects of this flexibility. Furthermore, OVOS is complementary to the atomic based generalized contraction scheme. If OVOS were applied to atoms described by large primitive basis sets, the resultant "atomic" orbitals would constitute another generalized contraction atomic orbital basis, but with a different criterion than the natural orbital approach of Almlöf and Taylor.⁴

Obviously, to obtain a general evaluation of the performance of the OVOS approach in different high-level correlated calculations, the method has to be thoroughly tested with respect to different features of the electron correlation effects. In addition to accurate calculations of molecular energies and geometries⁶ considerable attention is paid to the accurate determination of molecular properties.^{2,7-10} The basis set dimension problem in calculations of atomic and molecular properties becomes even more acute than for molecular energy hypersurfaces. Since the OVOS method retains the basis set flexibility at the molecular level it should also be suitable for calculations of highly correlated values of molecular properties. The purpose of this paper is to investigate different aspects of the performance of the OVOS approach in calculations of atomic and molecular electric

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properties. The dipole polarizability of the fluoride ion and the dipole moment and polarizability of HF are chosen as illustrative examples. The correlation effects and their dependence on the reduction of the virtual orbital space are investigated within the MBPT^{2,6–8,11,12} (through the fourth order) and CC^{2,10,13–19} (through the CCSDT-1 approximation^{16,17}) methods.

In Sec. II of this paper the OVOS method is briefly reviewed. Certain important computational details and the results obtained for electric properties of F⁻ and HF are presented in Sec. III and discussed from the point of view of the performance of the OVOS approach. The conclusions of this paper, which will further indicate⁵ the high efficiency of the OVOS method, are summarized in Sec. IV.

II. SURVEY OF THE OVOS APPROACH

A detailed account of the OVOS method and the computational strategy involved can be found in Ref. 5. In short, the method is based on the observation that the major part of the correlation energy is recovered in the second order with respect to the correlation perturbation operator. The second-order correlation energy E_2 is variationally bound by the Hylleraas functional I_2 I_3 :

$$J_2 = \langle \Phi_1 | H_0 - E_0 | \Phi_1 \rangle + 2 \langle \Phi_1 | V - E_1 | \Phi_0 \rangle \geqslant E_2, \quad (1)$$

where H_0 , Φ_0 , and E_0 are the reference (unperturbed) Hamiltonian, wave function, and energy, respectively. Similarly, V, Φ_1 , and E_1 denote the correlation perturbation operator, the first-order correlation correction to Φ_0 , and the first-order correlation energy, respectively. The minimization of Eq. (1) assumes an intermediate normalization of the exact wave function Ψ with respect to Φ_0 , so that

$$\langle \Phi_1 | \Phi_0 \rangle = 0. \tag{2}$$

For the sake of simplicity let us consider a closed-shell N electron system and let us assume Φ_0 in the form of a single SCF HF determinant. Then the sum of HF Hamiltonians is a natural choice for H_0 and Φ_1 can be expressed solely in terms of double substitutions in Φ_0^{24} :

$$\Phi_1 = \sum_{\substack{i>j\\a>b}} t_{ij}^{ab(1)} |_{ij}^{ab} \rangle, \tag{3}$$

where $|{}_{ij}^{ab}\rangle$ denotes a single determinant resulting from the substitution of a pair (i,j) of spin orbitals occupied in Φ_0 (holes: i,j,...) by a pair (a,b) of virtual SCF HF spin-orbitals (particles: a,b,...), and

$$t_{ij}^{ab(1)} = -\langle_{ij}^{ab}|V|\Phi_{0}\rangle/\langle_{ij}^{ab}|H_{0} - E_{0}|_{ij}^{ab}\rangle$$

$$= \frac{\langle ab||ij\rangle}{\epsilon_{i} + \epsilon_{j} - \epsilon_{a} - \epsilon_{b}}$$
(4)

are the corresponding amplitudes with $\{\epsilon_p\}$ referring to the SCF HF orbital energies of either holes (p=i,j) or particles (p=a,b). The two-electron integral $\langle ab \mid \mid ij \rangle$ includes the exchange part

$$\langle ab \mid \mid ij \rangle = \langle ab \mid ij \rangle - \langle ab \mid ji \rangle$$
 (5)

and its symbol corresponds to the standard bracket notation.

In some analogy to concepts employed in the MCSCF methods^{8(c),25} the available virtual space of the dimension

 N_v is partitioned into active $(N_{\rm va})$ and external $(N_{\rm ve})$ virtual subspaces. The initial set $\{\phi_a\}$ of N_v SCF HF orbitals is then unitarily transformed into a subset $\{\phi'_a\}$ $(\alpha=1,...,N_{\rm va})$ of active virtual orbitals:

$$\phi_{\alpha}' = \sum_{a} U_{a\alpha} \phi_{a}. \tag{6}$$

The required elements of the matrix U are determined by the minimization functional (1) with the trial function

$$\tilde{\Phi}_1 = \sum_{i < j}^{N_{\text{av}}} \sum_{\alpha < \beta} t_{ij}^{\alpha\beta(1)} |_{ij}^{\alpha\beta} \rangle. \tag{7}$$

As shown in Ref. 5 the transformation matrix U can be written in an exponential form²⁵:

$$\mathbf{U} = \exp(\mathbf{R}) \tag{8}$$

with

$$\mathbf{R} = -\mathbf{R}^{+}.\tag{9}$$

Since the rotations among either active virtual or external virtual orbitals do not affect J_2 , the rotation matrix \mathbf{R} can be chosen as⁵

$$\mathbf{R} = \begin{bmatrix} \phi_{\text{av,av}} - \mathbf{R}_{\text{av,ev}} \\ \mathbf{R}_{\text{ev,av}} & \phi_{\text{ev,ev}} \end{bmatrix}$$
 (10)

where the subscripts av and ev indicate the dimension of the respective block matrices (av: $N_{\rm av}$, ev: $N_{\rm v}-N_{\rm av}$).

According to Eq. (4) the amplitudes $t_{ij}^{\alpha\beta(1)}$ depend on $\mathbf{R}_{\text{ev,av}} = \mathbf{X}$ and thus the second-order energy functional can be expressed solely in terms of \mathbf{X} and integrals over the initial set of orbitals. The Taylor expansion of the second-order energy functional

$$J_2(\mathbf{X}) = \sum_{i < j} \{ J_{ij}^{(0)} + \mathbf{J}_{ij}^{(1)} \mathbf{X} + \frac{1}{2} \mathbf{X}^{\dagger} \mathbf{J}_{ij}^{(2)} \mathbf{X} + O(\mathbf{X}^3) \}$$
(11)

can be used to define a general Newton-Raphson minimization scheme. Actually, a two-step minimization of J_2 , which involves interchangably freezing either the amplitudes $t_{ij}^{\alpha\beta(1)}$ or the rotation matrix **R**, has been found very successful from the computational point of view. This two-step procedure resembles that proposed long ago for the optimization of MCSCF functions. The explicit formulas used at each of the two steps and the corresponding algorithm are described in Ref. 5. Following an SCF calculation, only a small subset of the transformed two-electron integrals $\langle ij||ab\rangle$ are required in T_2 . For all higher orders of MBPT or for CC theory, the OVOS set can be a drastically smaller number of functions

In the present paper the OVOS method is applied to the calculation of atomic and molecular electric properties. In the presence of the external electric field perturbation with the strength parameter λ the second-order energy functional becomes λ dependent. Suppose that some active virtual subspace of the dimension $N_{\rm av} \leqslant N_v$ has been selected for $\lambda=0$ and the matrix $\mathbf{X}^{(0)}=\mathbf{X}(\lambda=0)$ is determined. For $\lambda\neq 0$ and the same size of the active virtual subspace one can assume that

$$\mathbf{X}(\lambda) = \mathbf{X}^{(0)} + \lambda \, \mathbf{X}^{(1)} + \lambda^{2} \mathbf{X}^{(2)} + \cdots$$
 (12)

and the λ dependence of the functional $J_2(\lambda)$ determines the

 λ -dependent active virtual orbitals. The dependence of $J_2(\lambda)$ on the perturbation strength follows from the use of λ -dependent solutions of the HF problem, and

$$\phi_{\alpha}'(\lambda) = \sum_{a}^{N_{\nu}} U_{a\alpha}(\lambda)\phi_{a}(\lambda) = \phi_{\alpha}^{\prime(0)}$$

$$+ \lambda\phi_{\alpha}^{\prime(1)} + \lambda^{2}\phi_{\alpha}^{\prime(2)} + \cdots$$
(13)

can be determined analytically through any order in λ by using explicit derivatives of $J_2(\lambda)$ with respect to λ . This would be necessary if the perturbed active virtual orbitals were used in analytic calculations of correlation corrections to electric properties. 6,27 The same goal, at least for lowerorder electric properties (e.g., multiple moments and polarizabilities), can be achieved by using a numerical finite-field perturbation approach.^{7-9,28} Both the second-order energy functional $J_2(\lambda)$ and the resulting λ -dependent active virtual orbitals $\phi_{\alpha}(\lambda)$ are determined for some preselected small values of the perturbation strength parameter λ and then directly employed for the calculation of λ -dependent correlation energies. The correlation corrections to different properties associated with the given perturbation are obtained as the numerical derivatives of the λ -dependent correlation energies. With the current computational experience the numerical finite-field procedure^{7-10,29} can be made both efficient and accurate.

The reoptimization of the active virtual subspace in the presence of some external perturbation results in a set of λ dependent active virtual orbitals. Their composition considered in terms of the initial AO basis set depends on the character of the perturbation operator. Hence, given some set of virtual SCF orbitals of the dimension N_{ν} , the OVOS method will produce a set of $N_{av} \leq N_{v}$ perturbation-adapted active virtual orbitals. They will include the major portion of both the correlation and perturbation-induced polarization effects and should be suitable for calculations of the electron correlation contribution to different properties at higher levels of theory. 2,5,7-19 In this way the dimension of the virtual orbital space can be considerably reduced without a major loss in its flexibility. However, the suitable values of the ratio $N_{\rm av}/N_{\nu}$ are expected to be larger than those found in calculations of correlation energies.5

III. COMPUTATIONAL DETAILS AND RESULTS

The present study is aimed principally at the evaluation of the applicability of the OVOS procedure for the reduction of the virtual space dimension in calculations of atomic and molecular properties by using high-level correlated methods. ^{2,7-10,14-19} The fluoride ion polarizability and the dipole moment and polarizability of the HF molecule are selected as illustrative examples. The calculation of correlation corrections to electric properties is carried out at different levels of the MBPT method ⁷⁻¹¹ and in the CCSDT-1 ¹⁵⁻¹⁹ approximation

All calculations have been performed by using relatively large perturbation-adapted basis sets. The numerical finite-field perturbation technique discussed in Sec. II has been used to determine the field-dependent active virtual orbitals from field-dependent SCF orbitals. For both F^- and HF the

values of the external electric field strength employed in our calculations are $\lambda=\pm0.005$ a.u. The field-dependent active virtual orbitals obtained in the optimization procedure with several different choices of the active virtual subspace have then been used to calculate the field-dependent correlation energies $^{7-12}$ at various levels of theory. The numerical differentiation of these correlation energies leads finally to the required electron correlation corrections to the dipole moment of HF and dipole polarizabilities of F^- and HF. The investigation of these corrections in relation to the structure and size of the optimized virtual orbital space is the main objective of this paper.

A. The fluoride ion

Since the recognition of the importance of the electron correlation contribution to the dipole polarizability of F⁻,³⁰ several accurate calculations have been performed by using high-level correlated methods. 10,31-33 The most recent studies^{10,33} indicate that nearly 50% of the total polarizability follows from the electron correlation contribution. The present calculations do not aim at the highest accuracy of the final result and for this reason we employ a moderate GTO/ CGTO basis set generated from the (9.5) GTO set of van Duijneveldt³⁴ by using the basis set polarization method.³⁵ In order to allow for a proper description of the diffuse electron distribution in F⁻, the initial sp basis set is first augmented to (11.7) by geometrically generated s and p functions. The final polarized [11.7.4/6.4.3] GTO/CGTO basis set^{35,36} gives the SCF dipole polarizability of F⁻ equal to 10.49 a.u. as compared to the estimated Hartree-Fock limit of about 10.67 a.u. 10,30-33,37

The total virtual orbital space for the [11.7.4/6.4.3] basis set comprises 7s-, 3p-, and 3d-type shells and will be hereafter denoted as (7,3,3). Within the same notation the reduced optimized virtual orbital subspaces investigated in this paper correspond to (1,2,2), (0,2,1), and (0,1,1). Their dimension is 17, 11, and 8, respectively, compared to 31 virtual orbitals in the full virtual orbital space.

Both the active virtual orbital optimization and the calculation of correlation contributions have been carried out with uncorrelated ls and 2s atomic orbitals of F⁻. The contribution of these occupied orbitals to the dipole polarizability of the fluoride ion is negligibly small.³¹

The results of our calculations of the 2p shell correlation energy of F^- are presented in Table I. The high efficiency of the OVOS method is evident and the present data simply extend the list of applications of the OVOS approach to the calculation of correlation energies considered in Ref. 5. It has been suggested by Adamowicz and Bartlett⁵ that the total correlation energy at a given level of theory and for the given size of the active virtual orbital space can be estimated by using the full basis set values of the second-order correlation energy. Those are calculated anyway in the OVOS method and constitute the major part of the total correlation energy. The present values of the estimates of the MBPT(4) and CCSDT-1 correlation energies $\left[\widetilde{Q}_{\text{corr}}^{\text{MBTP}}(4)\right]$ and $\left[\widetilde{Q}_{\text{corr}}^{\text{CCSDT-1}}(1)\right]$ give additional support to this method based on the calculated OVOS higher-order contributions.

The dipole polarizability data for F⁻ are given in Table

TABLE I. OVOS study of the 2p-shell correlation energy of the fluoride ion. All values in a.u.

	Virtual space ^b								
Contribution/ method ^a	(7,3,3)° 31	(1,2,2) 17	(0,2,1) 11	(0,1,1)					
MBPT contribution	is to the 2p-shell correl	ation energy							
Q_1^D	– 0.171 036	- 0.170 500	- 0.162 559	- 0.160 987					
Q_3^D	+ 0.003 634	+ 0.003 441	+ 0.002 424	+0.001581					
Q.5	0.003 368	0.003 244	- 0.002 997	0.000 864					
Q_{4d}^D	- 0.001 934	0.001 828	- 0.001 738	- 0.001 320					
Q_{\bullet}^{T}	- 0.007 214	- 0.006 945	- 0.004 533	- 0.002 190					
$Q_{4d}^Q + Q_{4r}^D$	+ 0.002 247	+ 0.002 216	+ 0.001 746	+ 0.001 600					
Total 2p-shell corre	lation energy ^d								
$Q_{\text{corr}}^{\text{MBPT}}(2)$	- 0.171 036	- 0.170 500	- 0.162 559	- 0.160 987					
	(100.0)	(99.7)	(95.0)	(94.1)					
$Q_{\text{corr}}^{\text{MBPT}}(3)$	- 0.167 402	-0.167059	- 0.160 135	- 0.159 406					
	(100.0)	(99.8)	(95.7)	(95.2)					
$Q_{\text{corr}}^{\text{SDQ-MBPT}}(4)$	- 0.170 457	- 0.169 914	- 0.163 124	- 0.159 990					
	(100.0)	(99.7)	(95.7)	(93.9)					
$Q_{\text{corr}}^{\text{MBPT}}(4)$	- 0.177 671	- 0.176 870	- 0.167 651	- 0.162 181					
	(100.0)	(99.5)	(94.4)	(91.3)					
Q CCSDT-1	- 0.175 116	- 0.174 360	- 0.165 463	- 0.161 280					
	(100.0)	(99.6)	(94.5)	(92.1)					
Estimates of the 2p-	shell correlation energ	y ^{d,e}							
$\tilde{Q}_{\text{corr}}^{\text{MBPT}}(4)$	- 0.177 671	 0.177 406	- 0.176 128	- 0.172 230					
	(100.0)	(99.9)	(98.6)	(96.9)					
$\widetilde{Q}_{corr}^{CCSDT-1}$	0.175 116	- 0.174 896	- 0.173 940	- 0.171 329					
	(100.0)	(99.9)	(99.3)	(97.8)					

^{*}For definition of symbols used to denote different correlation contributions and different approximations for the total correlation energy see Refs. 7, 10, and 38.

II. At first sight the corresponding OVOS results do not appear to be so impressive as those for the correlation energy. In the latter case even the (0,1,1) optimized active virtual orbital space is capable of reproducing more than 90% of the full basis set correlation energy. In the case of the dipole polarizability this space gives less than 50% of the full basis set MBPT(4) and CCSDT-1 correlation corrections. On the other hand, this could have been anticipated from the very beginning since in the case of correlation corrections the given reduced space is simultaneously used to build the correlation perturbed functions and their field-perturbed components.^{7,12} For this reason it is obvious that the dimension of the OVOS in calculations of properties must be larger than that in calculations of correlation energies. Since only the first-order correlation correction to the wave function is directly optimized in the OVOS procedure, the dimension of the OVOS must be large enough to adequately reproduce the higher-order corrections. Those, as can be seen from the data of Table II, are needed in order to obtain sufficiently accurate contributions at the level of MBPT(4) and CCSDT-1 approaches.

It should be remarked, however, that the polarizability of fluoride is a rather specific and difficult case. The total correlation correction is very large and the fourth-order terms are very large as well; their sum being larger than the second-order correlation contribution to the dipole polarizability. Still reducing the dimension of the OVOS from 31 to 17 virtual orbitals saves 93.5% of the full basis set result in the MBPT(4) approximation. The estimated results, $\tilde{Q}_{\text{corr}}^{\text{MBPT}}(4)$ and $\tilde{Q}_{\text{corr}}^{\text{CCSDT-1}}$ are only marginally better than the corresponding $Q_{\text{corr}}^{\text{MBPT}}(4)$ and $Q_{\text{corr}}^{\text{CCSDT-1}}$ data.

The application of the OVOS method to the calculation of correlation corrections to the dipole polarizability of F⁻ has been selected in order to demonstrate that even in that case this approach can provide a considerable reduction of the virtual space dimension (from 31 to 17 orbitals) without a significant loss in the accuracy of the higher-level results. This occurs in spite of the fluoride ion polarizability being a rather specific and isolated case. More representative, from the point of view of the general applicability and usefulness of the OVOS method, are the results for the dipole moment and polarizability of the HF molecule.

^bThe symbol (n_1, n_2, n_3) means that n_1s , n_2p , and n_3d -type shells are retained in the virtual orbital space. The total number of active virtual orbitals is given underneath this symbol.

[&]quot;Total virtual orbital space corresponding to the [11.7.4/6.4.3] GTO/CGTO basis set used in present calculations.

^dThe SCF energy for the present basis set is — 99.448 202 a.u. The numbers in parentheses give the percentage of the corresponding full basis set result.

Estimated values obtained by using the full basis set second-order correlation energy and the higher-order corrections computed with a reduced virtual orbital space (Ref. 5).

TABLE II. OVOS study of the electron correlation contributions to the dipole polarizability of the fluoride ion. All values in a.u.

	Virtual space ^a							
Contribution/ method ^a	(7,3,3) ^a 31	(1,2,2) 17	(0.2.1) 11	(0,1,1)				
MBPT contributions to the 2	p-shell correlation energ			•				
Q_2^D	+ 4.83	+ 4.83	+ 4.75	+4.13				
Q_3^D	– 2.73	 2.71	— 2.44	-2.04				
03	+2.14	+ 1.85	+ 0.97	+ 0.27				
Q ₃ Q ₄ Q ₄ Q ₄ Q ₄	+ 0.83	+0.74	+0.54	+ 0.29				
o_I^T	+2.45	+2.31	+ 1.48	+ 0.67				
$Q_{4d}^Q + Q_{4r}^D$	- 0.19	- 0.19	- 0.11	- 0.05				
Total 2p-shell correlation cor	rection ^b							
$Q_{\text{corr}}^{\text{MBPT}}(2)$	+ 4.83	+ 4.83	+ 4.75	+4.13				
	(100.0)	(100.0)	(98.3)	(85.5)				
$Q_{\text{corr}}^{\text{MBPT}}(3)$	+ 2.10	+ 2.12	+2.31	+ 2.09				
	(100.0)	(101.0)	(110.0)	(99.5)				
$Q_{\rm corr}^{\rm SDQ-MBPT}(4)$	+ 4.88	+4.52	+ 3.71	+ 2.60				
	(100.0)	(92.6)	(76.0)	(53.3)				
$Q_{\rm corr}^{\rm MBPT}(4)$	+ 7.33	+6.85	+ 5.19	+ 3.27				
	(100.0)	(93.5)	(70.8)	(44.6)				
Q CCSDT-1	+ 6.42	+ 5.58	+ 4.18	+ 2.90				
	(100.0)	(86.9)	(65.1)	(45.2)				
Estimates of the 2p-shell corr	elation contribution ^c							
$\widetilde{Q}_{corr}^{MBPT}(4)$	+ 7.33	+6.85	+ 5.27	3.97				
	(100.0)	(100.0)	(71.9)	(54.2)				
$\widetilde{Q}_{\mathrm{corr}}^{\mathrm{CCSDT-1}}$	+6.42	+ 5.58	+4.26	3.60				
	(100.0)	(86.9)	(66.4)	(56.1)				

[&]quot;See the corresponding footnotes to Table I.

B. The HF molecule

The first- and second-order electric properties of the HF molecule have been widely studied over the past few years at different levels of theory. ^{7,8(c),38,39} Similarly as in the case of F⁻ the principal aim of this study is not to obtain the best values of the dipole moment and polarizability of HF but to investigate the performance of the OVOS method in highlevel correlated calculations of the electron correlation corrections to those electric properties.

We have performed two series of calculations of the dipole moment (μ) and dipole polarizability (α) of HF. The first, more comprehensive, series has been carried out by using a rather small GTO/CGTO basis set built of the fluorine basis set used in our calculations for F⁻ (see Sec. III A) and a [6.4/3.2] GTO/CGTO basis set for hydrogen. The latter has been generated from the (5) GTO basis set of van Duijneveldt³⁴ by using the basis set polarization scheme. ^{35,36} The SCF dipole moment (0.7542 a.u.) and dipole polarizability ($\alpha_{xx} = \alpha_1 = 4.49$ a.u., $\alpha_{zz} - \alpha_{\parallel} 5.72$ a.u.) obtained with this basis set (basis A) at the internuclear distance R = 1.7328 a.u. are very close to the corresponding near-Hartree–Fock data. ^{7,8(c),38-40}

The full space of virtual orbitals generated in SCF calcu-

lations with basis A comprises 18σ -, 8π -, and 3δ -type orbitals (40 virtual orbitals) and is denoted by the following symbol (18, 8, 3). It has been reduced by using the OVOS method first to the optimized active subspace (6,4,2) involving 18 virtual orbitals and then to the subspace of nine virtual orbitals (3,2,1). The energy data calculated at the level of MBPT(4) and CCSDT-1 methods for the internuclear distance R=1.7328 a.u. are presented in Table III. The corresponding dipole moment and polarizability results are collected in Table IV. In all correlated calculations no excitations are considered from the two lowest-energy occupied MOs of HF (primarily 1s and 2s orbitals of F). The dimension of the two optimized active virtual subspaces corresponds to about 50% and 25% of the total virtual orbital subspace.

As regards the total correlation energy data of Table III they demonstrate once again the very high efficiency of the OVOS method. About 95% of the MBPT(4) and CCSDT-1 correlation energy is recovered even with a very small OVOS comprising only nine virtual orbitals. This percentage is increased to about 99% by using the estimates based on the full space second-order correlation energy.

It follows from the results presented in Table IV that the reduction of the dimension of the active virtual orbital space

The SCF dipole polarizability calculated with the present [11.7.4/6.4.3] basis set is equal to 10.49 a.u.

Estimates of the 2p-shell correlation contribution to the dipole polarizability of F⁻ obtained by using the full basis set second-order corrections and the OVOS results for higher-order contributions.

TABLE III. OVOS study of the correlation energy of HF. Calculations with basis A at R = 1.7328 a.u. All values in a.u.

		Virtual space ^b		
Contribution/ method ^a	(18,8,3)° 40	(6,4,2) 18	(3,2,1)	
MBPT contribution	s to the correlation energy		· · · · · · · · · · · · · · · · · · ·	
Q_2^D	- 0.156 930	- 0.156 180	- 0.149 341	
Q ^P ₃ Q ^S ₄ Q ^D _{4d} Q ^T	- 0.002 729	- 0.002 956	-0.003913	
Q_4^S	- 0.001 197	- 0.000 845	- 0.000 509	
Q_{4d}^D	- 0.001 068	- 0.001 002	- 0.000 954	
Q_{A}^{T}	0.003 692	- 0.003 262	- 0.001 359	
$Q_{4d}^Q + Q_{4r}^D$	+ 0.001 890	+ 0.001 845	+ 0.001 529	
Total correlation en	ergy ^{d,e}			
$Q_{\text{corr}}^{\text{MBPT}}(2)$	- 0.156 930	- 0.156 180	- 0.149 341	
	(100.0)	(99.5)	(95.2)	
$Q_{\text{corr}}^{\text{MBPT}}(3)$	- 0.159 659	- 0.159 136	-0.153254	
	(100.0)	(99.7)	(96.0)	
$Q_{\rm corr}^{\rm SDQ-MBPT}(4)$	- 0.160 034	— 0.159 138	— 0.153 188	
	(100.0)	(99.4)	(95.7)	
$Q_{\rm corr}^{\rm MBPT}(4)$	- 0.163 726	- 0.162 400	— 0.154 547	
	(100.0)	(99.2)	(94.4)	
Q CCSDT-1	— 0.163 083	– 0.161 919	-0.154237	
	(100.0)	(99.3)	(94.6)	
	al correlation energyd,f			
$\tilde{Q}_{corr}^{MBPT}(4)$	-0.163726 -0	.163 150 — 0.162 136		
_	(100.0)	99.6) (99.0)		
$\widetilde{Q}_{ ext{corr}}^{ ext{CCSDT-1}}$	-0.163083 -0	.162 669 — 0.161 826		
	(100.0)	99.7) (99.2)		

See footnote a to Table I.

by about 50% has only a minor effect on the cacluated MBPT(4) and CCSDT-1 correlation correction to the dipole moment and polarizability of HF. A further reduction of the active virtual orbital space down to about 25% of the initial dimension results in recovering about 70% of the corresponding full space correlation corrections. Not too much is gained by using the estimates based on the full space values of the MBPT(2) results. In contrast to the correlation energy calculations the major loss in the correlation contribution to electric properties is due to the Q_4^S and Q_4^T terms rather than due to less accurate calculation of Q_2^D . Simply, one needs the OVOS flexible enough to provide a sufficiently accurate form of higher than the first-order correlated functions. Moreover, the dominance of the Q_2^D term is not that pronounced as in the case of the correlation energy. On the other hand, even the results obtained for the (3,2,1) OVOS, can be considered as reasonably good because of the relative smallness of the correlation corrections to μ and α .

The size of the total correlation corrections presented in Table IV with respect to the total dipole moment (about 6%) and the total polarizability (about 12% for α_{xx} and about 9% for α_{zz}) is quite representative for most closed-shell molecules. 7-9,29,31,38,39 Hence, a tremendous reduction

of the virtual orbital space in high-level correlated calculations of properties can be accomplished without significant loss of accuracy.

The second series of calculations of the dipole moment and polarizability of HF has been performed with a much larger basis set which has been previously employed in accurate MBPT(4) studies of this molecule.³⁹ This basis set, whose detailed description has been given elsewhere, ⁴¹ consists of a [12.8.3.1/8.5.3.1] GTO/CGTO set on F and a [7.2.1/4.2.1] GTO/CGTO set on H, and will be hereafter termed as basis B. In calculations at the correlated level the two lowest-energy occupied MOs have been frozen. The total virtual orbital space for basis B involves 62 orbitals with the partition into σ , π , δ , and ϕ symmetries given by the symbol (24,12,5,1). Three different optimized virtual orbital subspaces have been examined and the main results for the correlation energy, dipole moment, and dipole polarizability are collected in Table V.

The largest reduced OVOS, (20,11,5,1), is, in terms of its dimension ($N_{\rm av}=56$), a counter-part of a virtual orbital subspace which could have been obtained by deleting from the initial virtual orbital space six highest-energy orbitals (4 σ - and 1 π -type). In the present study the removal of those

^bThe symbol (n_1, n_2, n_3) gives the number of σ - (n_1) , π - (n_2) , and δ -type (n_3) optimized virtual orbitals. The total dimension of the OVOS is given below this symbol.

The full virtual orbital space for basis A.

^dExcitations from the two lowest-energy occupited orbitals of HF are not included.

The total SCF energy calculated for basis A is - 100.055 223 a.u.

See footnoe e to Table I.

TABLE IV. OVOS study of correlation corrections to the dipole moment (μ) and polarizability ($\alpha_{xx} = \alpha_1$), $\alpha_{zz} = \alpha_{\parallel}$) of the HF molecule. Calculations with basis A at the internuclear distance R = 1.7328 a.u. All values in a.u.

		μ Virtual space	ı	,	$lpha_{xx}$ Virtual space b		,	$lpha_{zz}$ Virtual space $^{ extsf{b}}$	
Contribution/method ^a	(18,3,3) ^a 40	(6,4,2) 18	(3,2,1)	(18,8,3) ^a 40	(6,4,2) 18	(3,2,1)	(18,8,3) ^a 40	(6,4,2) 18	(3,2,1)
MBPT contributions	to the correlation c	orrection ^a							
Q_2^D	- 0.0388	-0.0382	-0.0315	+0.671	+0.637	+0.622	+0.531	+0.514	+0.444
Q_3^D	+0.0065	+ 0.0064	+0.0050	- 0.215	- 0.194	- 0.165	-0.133	-0.122	-0.104
Q_4^S	-0.0053	- 0.0057	0.0020	+0.100	+0.076	+ 0.006	+0.082	+0.055	+0.019
Q_{4d}^D	-0.0024	-0.0024	- 0.0019	+0.027	+0.022	+0.015	+ 0.035	+0.030	+0.025
Q_4^T	-0.0069	- 0.0079	0.0024	+ 0.133	+ 0.124	+ 0.032	+ 0.110	+ 0.090	+ 0.033
$Q_{4d}^Q + Q_{4r}^D$	+ 0.0013	+0.0012	+0.0004	- 0.017	- 0.013	0.005	- 0.021	- 0.019	- 0.010
Total correlation corr	ections ^{a,b}								
$Q_{\rm corr}^{\rm MBPT}(2)$	-0.0388	-0.0382	-0.0315	+0.671	+0.637	+0.622	+0.531	+0.514	+0.444
	(100.0)	(98.5)	(81.2)	(100.0)	(94.9)	(92.7)	(100.0)	(96.8)	(83.6)
$Q_{\rm corr}^{\rm MBPT}(3)$	-0.0323	-0.0318	-0.0265	+0.456	+0.443	+0.457	+0.398	+0.392	+0.340
	(100.0)	(98.5)	(82.0)	(100.0)	(97.1)	(100.2)	(100.0)	(98.5)	(85.4)
$Q_{\text{corr}}^{\text{SDQ-MBPT}}(4)$	— 0.0387	-0.0387	-0.0300	+0.566	+0.528	+0.473	+ 0.494	+0.460	+0.374
	(100.0)	(100.0)	(77.5)	(100.0)	(93.3)	(83.6)	(100.0)	(93.1)	(75.7)
$Q_{\text{corr}}^{\text{MBPT}}(4)$	- 0.0456	0.0466	-0.0324	+0.699	+0.652	+0.505	+0.604	+0.550	+0.407
	(100.0)	(102.2)	(71.1)	(100.0)	(93.3)	(72.2)	(100.0)	(91.7)	(67.4)
Q CCSDT-1	-0.0437	 0.0442	-0.0318	+0.651	+0.608	+0.488	+0.567	+0.517	+0.396
	(100.0)	(101.1)	(72.8)	(100.0)	(93.4)	(75.0)	(100.0)	(91.2)	(69.8)
Estimates of the total	correlation correct	ions ^{a,c}							
$\tilde{Q}_{\text{corr}}^{\text{MBPT}}(4)$	-0.0456	-0.0472	-0.0397	+ 0.699	+0.686	+0.554	+0.604	0.567	0.494
_	(100.0)	(103.5)	(87.1)	(100.0)	(98.1)	(79.3)	(100.0)	(93.9)	(81.8)
$\widetilde{Q}_{corr}^{CCSDT-1}$	- 0.0437	- 0.0448	-0.0391	+0.651	+0.642	+0.537	+0.567	0.534	0.483
	(100.0)	(102.5)	(89.5)	(100.0)	(98.6)	(82.5)	(100.0)	(94.2)	(85.2)

^aSee the corresponding footnotes to Table III.

six orbitals is not based on a rather arbitrary criterion of orbital energies but follows directly from the minimization of the second-order energy functional. It is worthwhile to mention that the virtual orbitals which are almost completely removed by the OVOS method are not those with the highest orbital energies. As shown by the data of Table V, the reduction of the virtual orbital space to the (20,11,5,1) OVOS does not practically affect the calculated correlation corrections.

The second OVOS of the structure (10,6,3,0) corresponds to about 50% of the total set of virtual orbitals and its performance, for both the correlation energy and correlation corrections to electric properties of HF, is excellent. A further reduction of the number of explicitly used virtual orbitals to the (6,4,2,0) OVOS, i.e., to about one-fourth of the initial dimension, gives still more than 97% of the MBPT(4) and CCSDT-1 correlation energies and 83%–98% of the corresponding full basis set correlation contribution to properties.

A comparison of the basis A and basis B OVOS-results for correlation corrections to electric properties of HF shows that the size and flexibility of the initial basis set influence the values of $N_{\rm av}/N_{\nu}$ suitable for accurate calculations by using high-level correlated methods. A safe value of the ratio

 $N_{\rm av}/N_{\nu}$ seems to be close to 0.5 while for large initial basis sets it can be further reduced without a significant loss of accuracy. The determination of recommended values of this ratio for the given purpose and the given basis set requires a further exploration of the OVOS method.

It is known that the geometry dependence of molecular properties^{6,27(b),27(c),38} is an important factor which determines the final values to be compared with the experimental data. Hence, it is of some interest to investigate the performance of the OVOS method in calculations of the molecular property curves (surfaces). We have employed the OVOS method, followed by the MBPT(4) and CCSDT-1 calculations, for the determination of the dipole moment and polarizability curves of the HF molecule. The relevant quantities have been calculated at five internuclear distances (1.5828, 1.6828, 1.7328, 1.7828, and 1.8828 a.u.) in the vicinity of the experimental equilibrium bond distance (R = 1.7328a.u.)42 and then fitted to a fourth-degree polynomial. The distance dependence of different properties of the HF molecule is characterized in Table VI by a comparison of their derivatives evaluated at R = 1.7328 a.u.

The data presented in Table VI are obtained with the smaller (basis A) of the two basis sets which have already been used in this paper. Moreover, only the (6,4,2) OVOS is

The SCF results calculated with basis A are: $\mu = 0.7542$ a.u., $\alpha_{xx} = 4.488$ a.u., $\alpha_{zz} = 5.717$ a.u.

^eSee the corresponding footnote to Table II.

TABLE V. OVOS study of correlation corrections to the SCF energy and electric properties of the HF molecule. Calculations with basis B at the internuclear distance R = 1.7328 a.u. All values in a.u.

Virtual space					Correlation corrections ^a				
Property	Structureb	$N_{ m av}$	$Q_{\rm corr}^{\rm MBPT}(2)$	$Q_{\rm corr}^{\rm MBPT}(3)$	$Q_{\rm corr}^{\rm SDQ-MBPT}(4)$	Q MBPT (4)	Q CCSDT-1	$\widetilde{Q}_{\rm corr}^{ m MBPT}(4)^{ m c}$	Q̃ CCSDT-1c corr
Energy ^d	(24,12,5,1)°	62	- 0.175 809 (100.0)	- 0.175 985 (100.0)	- 0.176 295 (100.0)	- 0.181 170 (100.0)	- 0.180 637 (100.0)	- 0.181 170 (100.0)	- 0.180 637 (100.0)
	(20,11,5,1)	56	- 0.175 809 (100.0)	- 0.175 985 (100.0)	- 0.176 294 (100.0)	- 0.181 169 (100.0)	- 0.180 635 (100.0)	- 0.181 169 (100.0)	- 0.180 635 (100.0)
	(10,6,3,0)	28	- 0.175 090 (99.8)	- 0.175 492 (99.7)	- 0.175 692 (99.7)	- 0.180 384 (99.6)	- 0.179 898 (99.6)	- 0.181 103 (100.0)	- 0.180 617 (100.0)
	(6,4,2,0)	18	- 0.172 193 (97.9)	- 0.173 230 (98.4)	- 0.173 113 (98.2)	- 0.177 077 (97.7)	- 0.176 757 (97.9)	- 0.180 693 (99.7)	- 0.180 373 (99.9)
$\mu^{ exttt{d}}$	(24,12,5,1)	62	- 0.041 8 (100.0)	- 0.034 2 (100.0)	- 0.040 5 (100.0)	- 0.048 2 (100.0)	- 0.046 3 (100.0)	- 0.048 2 (100.0)	- 0.046 3 (100.0)
	(20,11,5,1)	56	- 0.041 8 (100.0)	- 0.034 2 (100.0)	- 0.040 5 (100.0)	- 0.048 2 (100.0)	- 0.046 3 (100.0)	- 0.048 2 (100.0)	- 0.046 3 (100.0)
	(10,6,3,0)	28	- 0.041 7 (99.8)	- 0.034 3 (100.3)	- 0.039 9 (98.5)	- 0.047 4 (98.3)	- 0.045 5 (98.3)	- 0.047 5 (98.5)	- 0.045 6 (98.5)
	(6,4,2,0)	18	- 0.39 6 (94.7)	- 0.032 7 (95.6)	- 0.037 9 (93.6)	- 0.044 8 (92.9)	- 0.043 2 (93.3)	0.047 0 (97.5)	0.045 4 (98.0)
$a_{xx} = a_1^{d}$	(24,12,5,1) ^e	62	+ 0.702 (100.0)	+ 0.449	+ 0.561 (100.0)	+ 0.719 (100.0)	+0.672 (100.0)	+ 0.719 (100.0)	+0.672 (100.0)
	(20,11,5,1)	56	+ 0.702 (100.0)	+ 0.449 (100.0)	+ 0.561 (100.0)	+ 0.719 (100.0)	+ 0.672 (100.0)	+ 0.719 (100.0)	+ 0.672 (100.0)
	(10,6,3,0)	28	+ 0.693 (98.7)	+ 0.447 (99.6)	+ 0.537 (95.7)	+ 0.686 (95.4)	+ 0.641 (95.4)	+ 0.695 (96.7)	+ 0.650 (96.7)
	(6,4,2,0)	18	+ 0.656 (93.4)	+ 0.434 (96.7)	+ 0.484 (86.3)	+ 0.596 (82.9)	+ 0.564 (83.9)	+ 0.642 (89.3)	+ 0.610 (90.8)
$\alpha_{xx}=lpha_{\parallel}{}^{d}$	(24,12,5,1) ^e	62	+ 0.553 (100.0)	+ 0.398	+ 0.493	+ 0.611 (100.0)	+ 0.578 (100.0)	+ 0.611 (100.0)	+ 0.578 (100.0)
	(20,11,5,1)	56	+ 0.553	+ 0.393	+ 0.492 (99.8)	+ 0.615	+ 0.579 (100.2)	+ 0.615 (100.7)	+ 0.579
	(10,6,3,0)	28	+ 0.544 (98.4)	+ 0.395	+ 0.476 (96.0)	+ 0.591 (96.7)	+ 0.555	+ 0.600 (98.2)	+ 0.564 (97.6)
	(6,4,2,0)	18	+ 0.511 (92.4)	+ 0.372 (93.5)	+ 0.429 (87.0)	+ 0.515 (84.3)	+ 0.490 (84.8)	+ 0.557 (91.2)	+ 0.532 (92.0)

^{*}See footnote a to Table I. The numbers in parentheses give the percentage of the corresponding full basis set result. All correlation corrections calculated without excitations from the two lowest-energy occupied MOs.

TABLE VI. OVOS study of derivatives of the total energy and electric properties of the HF molecule. MBPT(4) and CCSDT-1 results calculated with basis A. All values in a.u.

Derivative		Virtual space					
	Method	Full	OVOS*	OVOS est.b			
∂E ∂R	MBPT(4)	- 0.005 43	- 0.005 18	- 0.005 30			
	CCSDT-1	0.004 85	- 0.004 59	- 0.004 72			
$\frac{\partial^2 E}{\partial R^2}$	MBPT(4)	+ 0.636 96	0.604 50	0.625 40			
	CCSDT-1	0.636 07	0.612 13	0.625 29			
$\frac{\partial \mu}{\partial R}$	MBPT(4)	0.309	0.330	0.327			
	CCSDT-1	0.310	0.327	0.326			
$\frac{\partial \alpha_{xx}}{\partial R}$	MBPT(4)	1.53	1.78	1.72			
_	CCSDT-1	1.46	1.15	1.30			
$\frac{\partial \alpha_{22}}{\partial R}$	MBPT(4)	5.80	5.47	5.59			
	CCSDT-1	5.80	5.52	5.65			

[&]quot;The (6,4,2) OVOS as used in calculations presented in Tables I and II.

^bThe symbol (n_1, n_2, n_3, n_4) gives the numbers of σ -, π -, δ -, and ϕ -type orbitals included in the active virtual orbital subspace of the dimension $N_{\rm av}$.

Estimates of the total correlation correction based on the full basis set result for Q_2^p and the higher-order contributions calculated with the given OVOS.

^dThe SCF results for basis B are: E = 100.065593 a.u., $\mu = 0.7568$ a.u.

^{*}Full virtual orbital space for basis B.

^bEstimates obtained by using the second-order correlation corrections from the full basis set calculations.

studied by a comparison of the relevant data with those calculated in the full basis set. The total energy gradients calculated by using the OVOS method are very close to the corresponding full basis set results. The agreement is further improved for the estimated OVOS data which are based on the second-order correlation energy computed in the full basis set. A similar conclusion can be made for the second-order derivatives of the energy. These two factors indicate the potential of the OVOS approach in molecular geometry optimization at high-correlated levels of theory. ^{6,27}

With the present choice of the structure of OVOS the results for the first-order derivatives of properties do not appear to be as good as those for the energy derivatives. It is possible that a simultaneous action of two different perturbations (the external electric field and the geometry change) modifies the requirements with regard to the structure and size of the optimized virtual orbital space. On the other hand, taking into account that the OVOS data of Table VI have been obtained with about one-half of the initial set of virtual orbitals, the results are still encouraging.

IV. SUMMARY AND CONCLUSIONS

In this paper the applications of the OVOS method⁵ have been extended to calculations of atomic and molecular electric properties. In general, the method has been found nearly as efficient as in previous studies of molecular correlation energies.⁵ The reduction of the virtual orbital space by about 50% has a negligible effect on the accuracy of dipole moments and polarizabilities calculated by using high-level correlated methods.^{2,13-18} Reducing the dimension of the virtual orbital space to about one-fourth of the initial size still gives meaningful results. They can be to some extent improved by using the estimation scheme suggested in Ref. 5 and utilizing the full basis set second-order correlation corrections. This means that the range of applications of highlevel correlated methods is extended by the OVOS approach to systems at least 2-4 times larger than those which could have been accurately studied by using the full space of available SCF virtual orbitals.

The major advantage of the OVOS method follows from the fact that the "unimportant" virtual orbitals are deleted by using a systematic approach based on the variation formulation of the optimization procedure. Applying the same approach in the presence of some external perturbation embeddes automatically the perturbation (polarization) effects into the selected subspace of optimized virtual orbitals. Hence, the corresponding perturbation-dependent OVOS is suitable for calculations of correlation corrections to the relevant properties.

It is well recognized that accurate calculations of atomic and molecular properties require the use of both high-level correlated methods^{2,7-10} and large basis sets.^{7-10,31,38,39} With the standard choice of the virtual orbital space those two conditions can be satisfied only for very small systems. The results presented in this paper show that the OVOS method offers a plausible solution to this problem.

The choice of the structure of the OVOS, and to some extent, its size is rather well defined by the formulation of the OVOS method in terms of the second-order energy func-

tional. The active virtual orbital subspace comprises those linear combinations of the initial SCF virtual orbitals which are most efficient in lowering the second-order correlation energy. It has been assumed in our OVOS study of correlation corrections to electric properties that the same active virtual orbital space is suitable for calculations in the presence of the external perturbation. In principle, including some external perturbation operator in the Hamiltonian may also change the requirements with regard to both the size and composition of the OVOS. To some extent this appears to be indicated by lowering of the efficiency of the OVOS approach with the number of perturbations involved and the order of the calculated property. The analysis of the occupation numbers of approximate natural orbitals which follow from the minimization of the J_2 functional can be used to make the choice of the OVOS suitable for the given property.

The conclusions made in Ref. 5 with regard to the usefulness of the OVOS scheme in accurate, high-level correlated calculations of molecular energies are supplemented by the present results for the derivatives of the total molecular energy. Since the geometry optimization by using high-level correlated methods^{27(b),27(c)} is usually the most time-consuming part of all calculations, the OVOS approach offers a new step in accurate predictions of molecular geometries.

Recently there have been some attempts to reduce the basis set size in high-level correlated calculations of molecular energies and properties. And In comparison with the OVOS method, neither of those approaches determines the virtual orbital space directly at the molecular level. The active virtual orbital subspace determined by the OVOS method is unique for the given molecule. This method does permit the use of very large atomic basis sets at the SCF level and saves the basis set flexibility at the molecular level. This feature of the OVOS approach might become particularly important in calculations of molecular geometries and properties.

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