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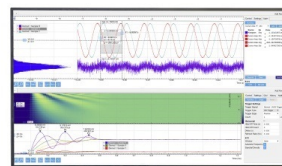
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Third-order multireference perturbation theory: The n -electron valence state perturbation-theory approach

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A formulation of the n -electron valence state perturbation theory (NEVPT) at the third order of perturbation is presented. The present implementation concerns the so-called *strongly contracted* variant of NEVPT, where only a subspace of the first-order interacting space is taken into account. The resulting strongly contracted NEVPT3 approach is discussed in three test cases: (a) the energy difference between the 3B_1 and 1A_1 states of the methylene molecule, (b) the potential-energy curve of the N_2 molecule ground state, and (c) the chromium dimer (Cr_2) ground-state potential-energy profile. Particular attention is devoted to the last case where large basis sets comprising also h orbitals are adopted and where remarkable differences between the second- and third-order results show up. © 2006 American Institute of Physics. [DOI: 10.1063/1.2148946]

I. INTRODUCTION

Multireference perturbation theory (MRPT) is nowadays a standard tool for the treatment of the dynamical correlation in quasidegenerate systems where more than one electronic configuration play an important role in the qualitative description of the wave function, as occurs, for instance, in molecules at geometries far from the equilibrium one (rupture of a chemical bond, transition states) or in most electronically excited states. A usual strategy to deal with quasidegenerate systems is to describe the zero-order wave function through a complete active space self consistent field¹ (CASSCF) calculation to take into account the static correlation and to improve the result by employing second-order perturbation theory (PT) to recover the dynamical correlation of the electrons. Among the most successful implementations the CASPT2 technique of Roos and coworkers stands out,^{2,3} where the first-order correction to the wave function is carried out in terms of internally contracted (IC) functions. More recently the n -electron valence state perturbation theory (NEVPT2),⁴⁻⁷ still based on an IC functions expansion, has been implemented and successfully tested.⁸ The main difference between CASPT2 and NEVPT2 lies in the choice of the zero-order Hamiltonian, mono-electronic (Focklike) in the former, and bi-electronic in the latter. One of the merits of NEVPT2 is the complete removal of intruder states without any need of resorting to the use of unphysical level shifts common to most preceding MRPT approaches.

Usually MRPT is carried out at the second order of perturbation in the energy. Often, however, in order to judge on

the efficiency and stability of the MRPT, it would be desirable to push the perturbation order at least one step further. **Since the third-order energy contribution makes use of exactly the same correction functions as are used in the construction of the first-order correction to the wave function, the implementation of a third-order MRPT appears to be feasible without excessive computational efforts.** Actually, versions of third-order MRPT have already been published by various authors: Werner⁹ in 1996 provided a version of CASPT3 employing a mixed basis of IC functions and simple configurations, Havenith *et al.*¹⁰ in 1999 and two of the present authors¹¹ in 2002 generated third-order MRPT based on configurations as expansion functions.

The present article is devoted to the description of the third-order implementation within the scheme of NEVPT with the adoption of IC functions throughout the perturbation series. The rest of the paper is organized as follows. Section II describes the third-order implementation after recalling the main features of the NEVPT technique. Section III is dedicated to the application of NEVPT3 to a few significant test cases (the CH_2 singlet-triplet splitting, the N_2 ground-state potential-energy curve, and the chromium dimer potential curve, with particular emphasis on the last case). Section IV contains some conclusive remarks.

II. NEVPT3

It is a well-known result of standard Rayleigh-Schrödinger PT that the third-order correction to the energy of a given state Ψ_m only necessitates the first-order correction to the wave function,

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$$E_m^{(3)} = \langle \Psi_m^{(1)} | V | \Psi_m^{(1)} \rangle - E_m^{(1)} \| \Psi_m^{(1)} \|^2. \quad (1)$$

If $\Psi_m^{(1)}$ has been obtained as an expansion over a given set of correction functions Φ_L ($\Psi_m^{(1)} = \sum_L c_L^{(1)} \Phi_L$), evaluation of $E_m^{(3)}$ is then straightforward provided the matrix elements of the perturbation operator $\langle \Phi_K | V | \Phi_L \rangle$ can be easily calculated. In NEVPT (Refs. 4 and 6) the zero-order wave function and energy $\Psi_m^{(0)}$ and $E_m^{(0)}$ are the solution of a CAS–configuration-interaction (CI) (usually CASSCF) equation $P_S H P_S \Psi_m^{(0)} = E_m^{(0)} \Psi_m^{(0)}$ with $P_S = \sum_K |K\rangle \langle K|$ denoting the projector onto a given CAS space S spanned by the determinants $|K\rangle$. The other zero-order wave functions not belonging to the CAS space, referred to as the correction functions or also as the “perturbers,” are of multireference nature and belong to CAS–CI spaces with well-defined occupation patterns of the core and virtual orbitals (collectively called the “inactive” orbitals) and with a given number of active electrons. The perturbers are indicated as $\Psi_{l,\mu}^{(k)}$ and the CAS–CI spaces they belong to as $S_l^{(k)}$ with k the number of electrons promoted to (if positive) or removed from (if negative) the active space and with l designating the occupation pattern of the inactive orbitals (μ simply enumerates the various perturbers). Only eight types of $S_l^{(k)}$ spaces have to be considered for the construction of $\Psi_m^{(1)}$: indicating with i, j indices for core orbitals (always doubly occupied in the CAS determinants), r, s for virtual orbitals (never occupied), and a, b, c for active orbitals (with all possible occupations), the $S_l^{(k)}$ spaces are spanned by doubly excited IC functions,

$$S_{ij,rs}^{(0)} \ni E_{ri} E_{sj} \Psi_m^{(0)},$$

$$S_{ij,r}^{(+1)} \ni E_{ri} E_{aj} \Psi_m^{(0)},$$

$$S_{rs,i}^{(-1)} \ni E_{ri} E_{sa} \Psi_m^{(0)},$$

$$S_{ij}^{(+2)} \ni E_{ai} E_{bj} \Psi_m^{(0)},$$

$$S_{rs}^{(-2)} \ni E_{ra} E_{sb} \Psi_m^{(0)},$$

$$S_{r,i}^{(0)} \ni E_{ri} E_{ab} \Psi_m^{(0)} \quad \text{and} \quad E_{rb} E_{ai} \Psi_m^{(0)},$$

$$S_i^{(+1)} \ni E_{ai} E_{bc} \Psi_m^{(0)},$$

$$S_r^{(-1)} \ni E_{ra} E_{bc} \Psi_m^{(0)}.$$

The E operators above are the spin-traced replacement operators¹² $E_{wx} = a_{w\alpha}^+ a_{x\alpha} + a_{w\beta}^+ a_{x\beta}$. Two variants of NEVPT have so far been implemented to the second order: the simpler one, called “strongly contracted” (SC-NEVPT2), makes use of exactly one perturber function from each $S_l^{(k)}$ subspace, obtained as a projection $\Psi_l^{(k)} = P_{S_l^{(k)}} H \Psi_m^{(0)}$. A second variant, called “partially contracted” (PC-NEVPT2) consists in the diagonalization of a model Hamiltonian within each subspace and is fully described in Ref. 6. We simply recall that both variants yield quite similar results in all the test cases so far examined. For this reason, in the development of the third-order NEVPT we have confined ourselves to the simpler variant, the strongly contracted approach (SC-

NEVPT3). The energies of the strongly contracted perturber functions are given by a Rayleigh ratio,

$$E_l^{(k)} = \frac{\langle \Psi_l^{(k)} | H^D | \Psi_l^{(k)} \rangle}{\langle \Psi_l^{(k)} | \Psi_l^{(k)} \rangle},$$

where H^D is a model Hamiltonian proposed by Dyall,¹³ mono-electronic in the core and virtual orbitals and fully bielectronic in the active orbitals

$$H^D = H_i + H_v + C,$$

$$H_i = \sum_{i,j} f_{ij} E_{ij} + \sum_{r,s} f_{rs} E_{rs},$$

$$H_v = \sum_{a,b} h_{ab}^{\text{eff}} E_{ab} + \frac{1}{2} \sum_{a,b,c,d} \langle ab | cd \rangle (E_{ac} E_{bd} - \delta_{bc} E_{ad}).$$

In the equations above, f_{ij} and f_{rs} are generalized Fock matrices,¹⁴ h_{ab}^{eff} is the matrix element of the one-electron part of the Hamiltonian corrected with the mean-field interaction with the core electrons and C is a suitable constant which makes H^D equivalent to H within the CAS space. The first-order correction to the wave function in the strongly contracted approach can be finally written as

$$\Psi_m^{(1)} = \sum_{l,k} c_l^{(k)} \Psi_l^{(k)}, \quad (2)$$

where the $\Psi_l^{(k)}$ functions are here assumed to be properly normalized and where the explicit form of the expansion coefficients for all the occurrences of the $S_l^{(k)}$ spaces is given in Ref. 6. Once the expression of $\Psi_m^{(1)}$ is known, it is possible to deal with the third-order formula given in Eq. (1), which reduces to

$$E_m^{(3)} = \langle \Psi_m^{(1)} | V | \Psi_m^{(1)} \rangle, \quad (3)$$

since the first-order contribution to the energy is null in NEVPT. The zero-order Hamiltonian is given by its spectral decomposition,

$$H_0 = \sum_{m'}^{\text{CAS}} |\Psi_{m'}^{(0)}\rangle E_{m'}^{(0)} \langle \Psi_{m'}^{(0)}| + \sum_{k,l} |\Psi_l^{(k)}\rangle E_l^{(k)} \langle \Psi_l^{(k)}|, \quad (4)$$

and the working equation for SC-NEVPT3 becomes

$$E_m^{(3)} = \sum_{l,k} \sum_{l',k'} c_{l'}^{(k')*} c_l^{(k)} \langle \Psi_{l'}^{(k')} | H - H_0 | \Psi_l^{(k)} \rangle, \quad (5)$$

where H_0 gives nonvanishing contributions only in the diagonal case ($l, k = l', k'$).

Given the form of the perturbers $\Psi_l^{(k)}$ which consist in linear combinations of doubly excited IC functions, the main difficulty in the implementation of Eq. (5) lies in the evaluation of the matrix elements of the Hamiltonian operator between two IC functions. This problem has been addressed in Refs. 15 and 16, where the matrix elements are produced by the symbolic program FRODO (after formal reduction of density operators) written in the computer algebra system MUPAD.¹⁷ Actually the FRODO program yields a FORTRAN subroutine for all occurrences of IC functions in the bracket of Eq. (5). In practice, no new quantities are necessary with

respect to those required in a NEVPT2 calculation; in particular, the highest particle rank of the density matrix which is required in Eq. (5) is four, exactly like in NEVPT2. The FORTRAN code implementing the third-order SC-NEVPT3 has been written in a parallelized version, using the “message passing interface”¹⁸ since the third-order formulas naturally lend themselves to a distributed calculation.

III. TEST CALCULATIONS

A. CH₂

The energy difference between the ³B₁ and the ¹A₁ states in methylene represents a classical test case for new calculation methods. For this molecule a full CI calculation was performed by Bauschlicher and Taylor¹⁹ using a double zeta plus polarization atomic basis set. Our second-order NEVPT results, already partially published elsewhere,⁸ both in the strongly and partially contracted variants, as well as the third-order SC-NEVPT3 calculations, are reported in Table I and compared with other calculations. Three different CAS spaces of increasing size are considered, the simplest of which corresponds to the distribution of the six valence electrons over the six valence orbitals. The third-order correction is rather conspicuous in the smallest active space, bringing a variation in the energy difference of -0.66 kcal/mol with respect to SC-NEVPT2. For the larger active spaces the correction is smaller, amounting to $+0.58$ kcal/mol for the 4220 space and $+0.15$ kcal/mol for the 7331 space. The comparison with the other third-order calculations, viz., the CASPT3 of Werner⁹ and the Møller-Plesset barycentric (MPB3) and Epstein-Nesbet (EN3) of Ref. 11, shows that the third-order results are all rather similar, with CASPT3 and NEVPT3 differing by 0.21 kcal/mol in the 3210 space, by 0.13 kcal/mol in 4220 and 0.06 kcal/mol in the 7331 space.

B. N₂

The potential-energy curve of the N₂ molecule in its ground state constitutes a good test case for MRPT due to the difficulties which may be encountered in the description of the dissociation of the triple bond. The basis set employed in the calculations is Dunning’s correlation consistent valence quadruple zeta²⁰ (cc-pVQZ) and the zero-order wave function is provided by a CASSCF calculation, carried out with the DALTON program,²¹ with the ten valence electrons distributed over the eight valence orbitals ($2s$ and $2p$). The second-order (SC-NEVPT2 and PC-NEVPT2) as well as the third-order (SC-NEVPT3) results are set out in Fig. 1 where the absolute energies are reported versus the internuclear distance. At the scale of Fig. 1 the results of PC-NEVPT2 are hardly distinguishable from those of SC-NEVPT2, the former lying slightly below the latter according to the general behavior of the two variants of NEVPT2 proved in Ref. 6. The third-order SC-NEVPT3 energy curve is located below the second-order curves and runs roughly parallel to them with an energy difference of about 0.03 a.u. Figure 2 reports again the potential-energy curves with the zero of the energy taken at the asymptotic value of dissociation for each

TABLE I. Energies for the CH₂ molecule.

Method	¹ A ₁ energy (a.u.)	¹ A ₁ energy (a.u.)	ΔE (kcal/mol)
3210 active space ^a			
CASSCF	-38.945 529	-38.965 954	12.82
CASPT2 ^b	-39.013 092	-39.037 695	15.44
CASPT3 ^b	-39.023 374	-39.043 766	12.80
MPB2 ^c	-39.011 695	-39.036 885	15.81
EN2 ^c	-39.024 854	-39.048 424	14.79
MPB3 ^c	-39.021 887	-39.042 750	13.09
EN3 ^c	-39.023 624	-39.043 291	12.34
SC-NEVPT2 ^d	-39.006 707	-39.028 498	13.67
PC-NEVPT2 ^d	-39.007 802	-39.029 354	13.52
SC-NEVPT3 ^d	-39.019 488	-39.040 216	13.01
4220 active space ^a			
CASSCF	-38.968 726	-38.982 788	8.82
CASPT2 ^b	-39.017 120	-39.038 707	13.54
CASPT3 ^b	-39.024 593	-39.044 195	12.30
MPB2 ^c	-39.016 396	-39.038 139	13.64
EN2 ^c	-39.024 499	-39.046 250	12.47
MPB3 ^c	-39.023 789	-39.044 005	12.69
EN3 ^c	-39.025 216	-39.044 839	12.31
SC-NEVPT2 ^d	-39.013 487	-39.032 376	11.85
PC-NEVPT2 ^d	-39.014 521	-39.033 006	11.60
SC-NEVPT3 ^d	-39.022 179	-39.041 994	12.43
7331 active space ^a			
CASSCF	-39.009 906	-39.029 672	12.40
CASPT2 ^b	-39.023 760	-39.043 345	12.29
CASPT3 ^b	-39.025 954	-39.045 359	12.18
MPB2 ^c	-39.024 489	-39.044 125	12.32
EN2 ^c	-39.026 107	-39.045 722	12.31
MPB3 ^c	-39.025 951	-39.045 521	12.28
EN3 ^c	-39.026 187	-39.045 699	12.24
SC-NEVPT2 ^d	-39.024 296	-39.043 529	12.07
PC-NEVPT2 ^d	-39.024 671	-39.043 843	12.03
SC-NEVPT3 ^d	-39.025 725	-39.045 202	12.22
Full CI ^e	-39.027 284	-39.046 348	11.96

^aPartition of the active space orbitals in the A₁, B₁, B₂, and A₂ symmetries.

^bReference 9.

^cReference 11.

^dThis work.

^eReference 19.

TABLE II. Spectroscopic properties of the ¹Σ_g⁺ ground state of N₂.

Method	r _e (Å)	D _e (eV)	ω _e (cm ⁻¹)	x _e ω _e (cm ⁻¹)
CASSCF ^a	1.1039	9.233	2337.1	13.68
CASPT2 ^b	1.1023	9.37	2332.6	14.51
CASPT3 ^b	1.1011	9.59	2350.7	14.09
SC-NEVPT2 ^a	1.1027	9.649	2332.6	14.10
PC-NEVPT2 ^a	1.1023	9.744	2336.0	14.17
SC-NEVPT3 ^a	1.1029	9.536	2331.3	14.17
Expt. ^c	1.098	9.906	2358.6	14.3

^aThis work.

^bReference 9.

^cReference 33.

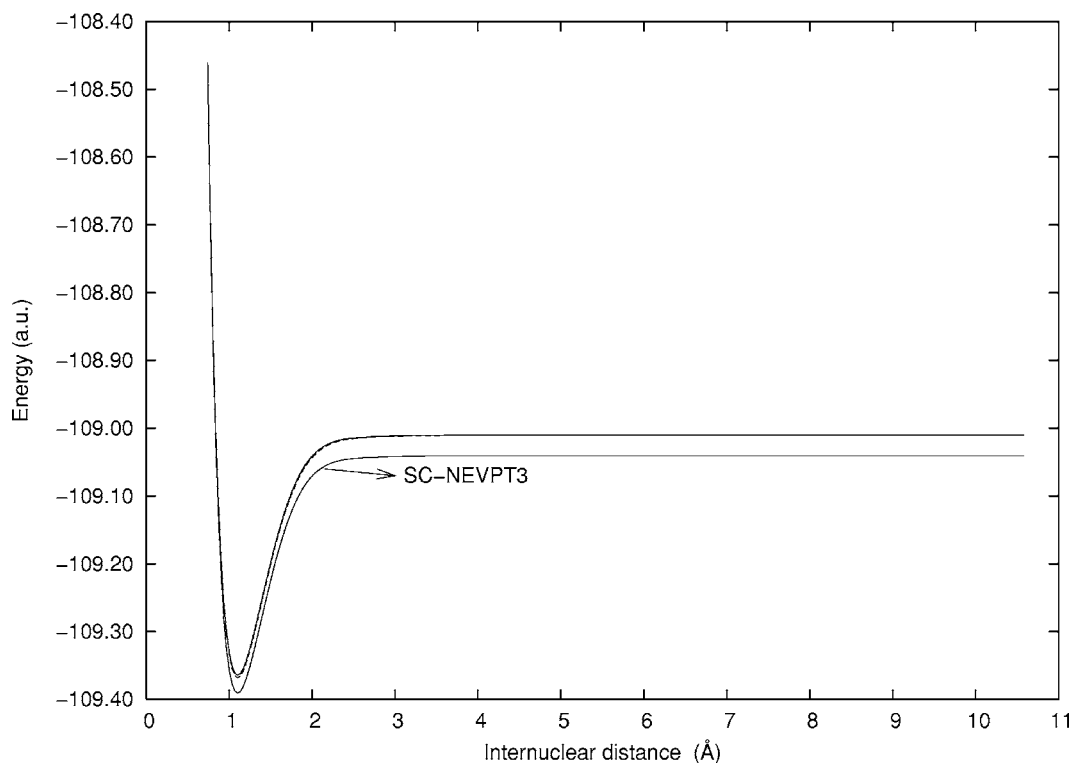


FIG. 1. Calculated potential-energy curves for the N_2 ground state: absolute energies.

curve. As can be seen from Fig. 2, no substantial change in the description of the potential-energy curve is brought about by the third-order calculation. Such a conclusion is also borne out by the comparison of some spectroscopic constants calculated with the three curves by numerical solution of the vibrational Schrödinger equation, reported in Table II.

C. Cr_2

The description of the potential-energy curve for the ground state of the chromium dimer stands out as a remarkably difficult task for *ab initio* methods. The interplay between the high number of quasidegenerate structures that are

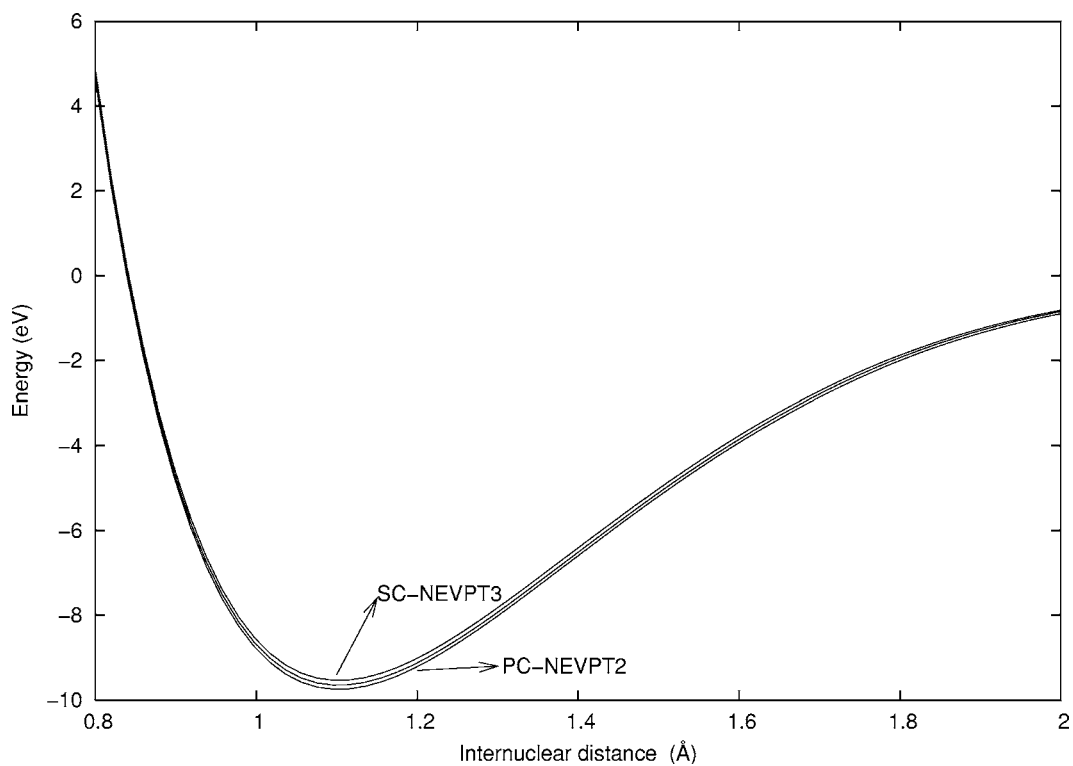


FIG. 2. Calculated potential-energy curves for the N_2 ground state: relative energies.

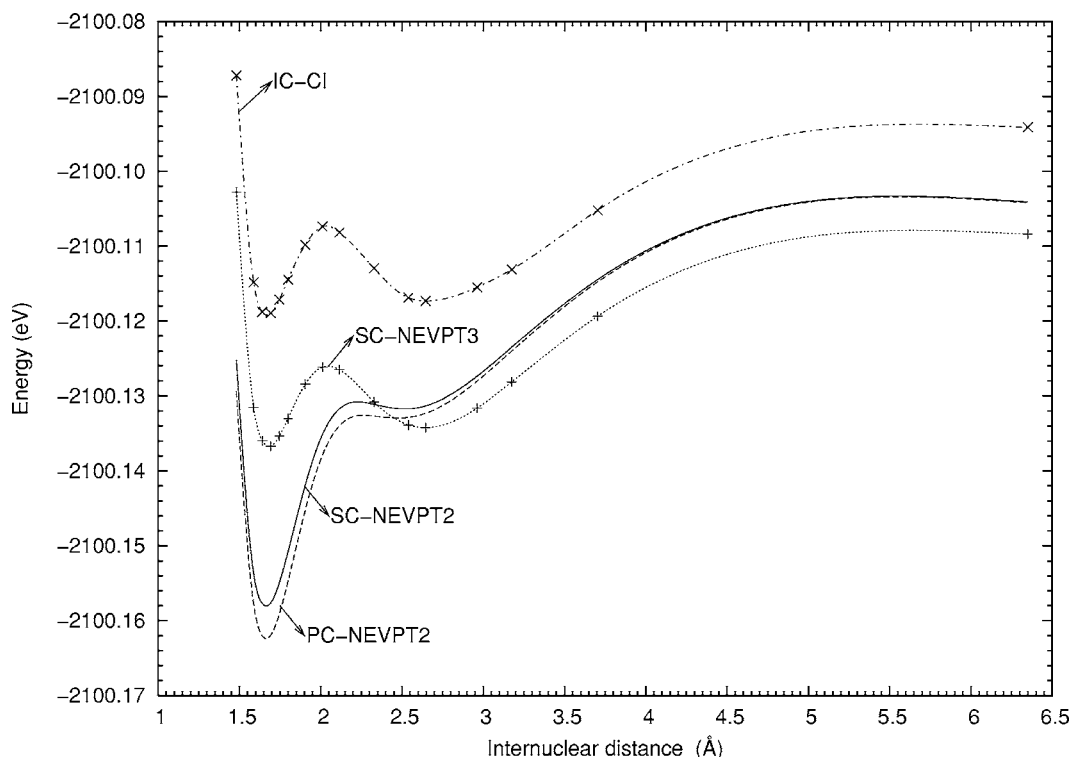


FIG. 3. Calculated potential-energy curves for the Cr_2 ground state in the ANO-L basis set: absolute energies.

necessary to qualitatively account for a correct dissociation to the high spin (septet) atoms, the great need for dynamical correlation required by the $3p$ and $3d$ orbitals which contend the same physical space and the presence of two distinct bond regions due to the $3d$ - $3d$ and $4s$ - $4s$ interactions, altogether contribute to make this little molecule a most complicated example of chemical bond. A recent work of Celani *et al.*²² gives a good survey of the literature concerning both theoretical and experimental results for the Cr_2 molecule. In the previous studies carried out by our group^{5,6} on the chromium dimer with the NEVPT2 technique, on one hand, good results were obtained for the equilibrium distance as well as for the dissociation energy, while, on the other hand, less satisfactory results were reached for the spectroscopic properties of $\Delta G_{1/2}$ and ω_e , due to the too sharp curvature of the calculated potential-energy function. In this section we take up the calculation of the Cr_2 curve both at the second and at the third order within the NEVPT approach, by adopting two ANO basis sets of different size; the first basis is the ANO-L set developed by Pou-Amerigo *et al.*²³ with the contraction scheme $21s15p10d6f4g \rightarrow [7s6p5d4f3g]$. All the results obtained with this basis set have been corrected for the basis set superposition error (BSSE) with the counterpoise method of Boys and Bernardi,²⁴ furthermore a relativistic correction has been introduced by simply adding the first-order contributions due to the mass-velocity and Darwin operators. The other basis is a larger ANO set, called ANO-RCC, recently developed by Roos^{25,26} and available at the MOLCAS internet site,²⁷ which includes also h atomic orbitals; the contraction scheme we adopted is $21s15p10d6f4g2h \rightarrow [10s10p8d6f4g2h]$. The basis set was optimized by the developers within the Douglas-Kroll Hamiltonian²⁸ so as to

account for the scalar relativistic effects. Our molecular calculations have consequently also been carried out including the Douglas-Kroll operator at the CASSCF level. No attempt to correct the results for the BSSE was deemed to be worth doing with this large basis set. In all cases, the CASSCF wave function was calculated by including all the $4s$ and $3d$ electrons and orbitals in the construction of the active space (12 active electrons in 12 active orbitals) and the perturbation calculations only took into account the $3s$ and $3p$ orbitals for the core correlation, keeping the more internal orbitals frozen. The zero-order CASSCF wave function was calculated with the MOLCAS program.²⁹ The evaluation of the SC-NEVPT3 energy, especially with the ANO-RCC basis (360 atomic orbitals) is rather a large calculation and has been carried out with a parallel architecture of 64 processors (Intel Xeon 3.0 Ghz) on an IBM CLX/1024 Linux cluster at the Italian supercomputer center CINECA. For a single point with the ANO-RCC basis the calculation used up about 2 h of clock time.

Figures 3 and 4 show the potential-energy curves calculated with the ANO-L basis; Fig. 3 presents the absolute energies while Fig. 4 shows the energies measured from the asymptotic values. As is apparent, the third-order contributions introduce large modifications to the picture obtained at the second order. The position of the minimum remains nearly the same but the value of the minimum is shifted upwards by a large amount (≈ 0.7 eV). Furthermore, the region of the $4s$ - $4s$ bond drastically changes nature at the third order, giving rise to a distinct outer minimum at $R = 2.6434$ Å. In order to ascertain whether such behavior could be attributed to deficiencies in the way the third-order correction takes into account the perturber functions in the

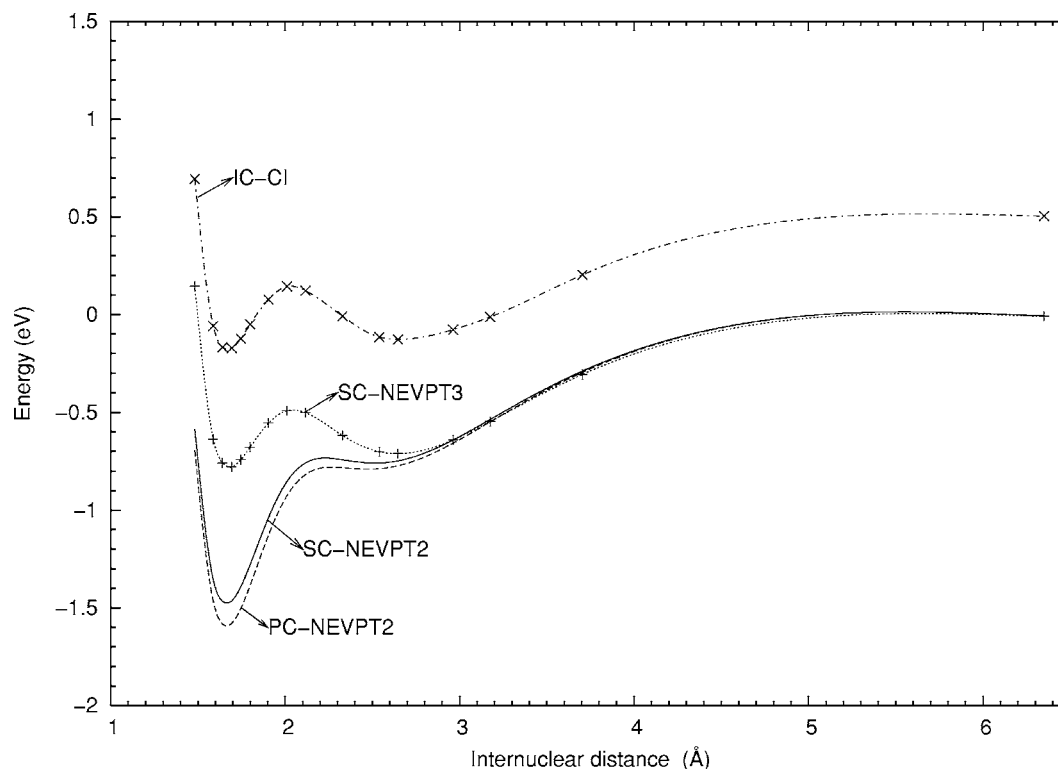


FIG. 4. Calculated potential-energy curves for the Cr_2 ground state in the ANO-L basis set: relative energies.

first-order interacting space, a completely variational calculation is shown in Figs. 3 and 4 where all the perturber functions $\Psi_l^{(k)}$ are included in the construction of a variational wave function $\Psi_m = a_0 \Psi_m^{(0)} + \sum_{l,k} a_l^{(k)} \Psi_l^{(k)}$, with the coefficients and the energy obtained by diagonalization of the corresponding Hamiltonian matrix. In order to partially correct for the size consistency error (SCE), Davidson's procedure³⁰ was applied but, despite such a correction, the SCE remained conspicuous. Such variational calculations, which belong to the family of internally contracted configuration interactions (IC-CIs),³¹ yielded a curve which runs roughly parallel to the third-order one, thus showing that the SC-NEVPT3 calculations are not affected by substantial error in the neglect of higher-order contributions deriving from the first-order inter-

acting space. Figures 5 and 6 show the calculations performed at the second and third order with the larger ANO-RCC basis set. The results are qualitatively similar to those obtained with the smaller basis but some significant quantitative differences can be remarked. The main characteristics of the calculations are collected in Table III. At the second order of perturbation the main difference which can be remarked passing from the smaller to the larger basis concerns the magnitude of the dissociation energy, which passes from a seemingly good value of 1.48–1.60 eV (experimental estimates range between 1.45 and 1.56 eV) to an “overshot” value of 1.70–1.82 eV. Similar results are obtained by Celani *et al.*²² for their CASPT2 studies, where a basis set limit for the dissociation energy is estimated to be ≈ 1.9 eV.

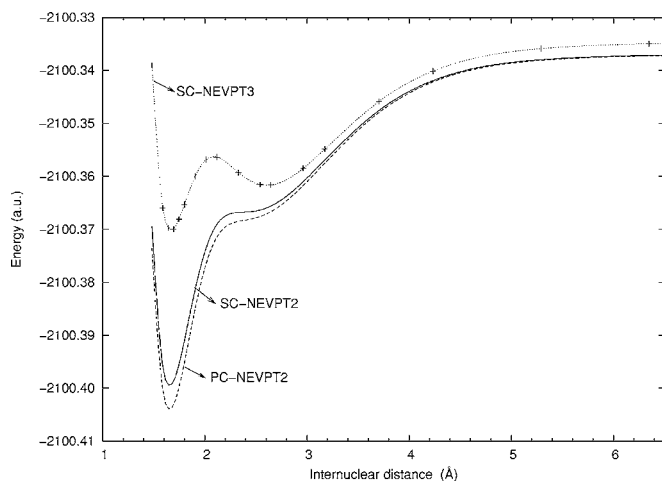


FIG. 5. Calculated potential-energy curves for the Cr_2 ground state in the ANO-RCC basis set: absolute energies.

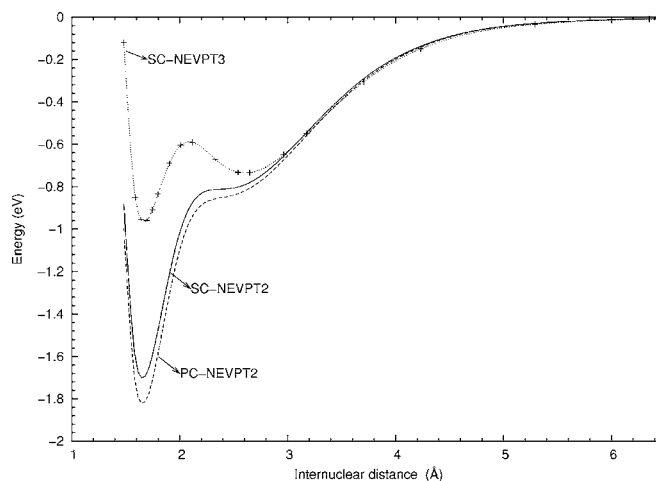


FIG. 6. Calculated potential-energy curves for the Cr_2 ground state in the ANO-RCC basis set: relative energies.

TABLE III. Characteristics of the calculated Cr₂ potential-energy curve.

Method		r_{in} (Å)	r_{out} (Å)	D_e (eV)	$\Delta G_{1/2}$ (cm ⁻¹)
ANO-L	SC-NEVPT2	1.6650	...	1.476	565.6
	PC-NEVPT2	1.6643	...	1.592	583.1
	SC-NEVPT3	1.6826	2.6434	0.780	383.6
	IC-CI	1.6692	2.6486	0.747	221.5
ANO-RCC	SC-NEVPT2	1.6551	...	1.702	579.7
	PC-NEVPT2	1.6551	...	1.822	587.5
	SC-NEVPT3	1.6711	2.6053	0.966	490.8
	Expt.	1.679 ^a	...	{ 1.45 ^b 1.56 ^d }	452 ^c

^aReference 34.^bReference 35.^cReference 36.^dReference 37.

The third-order results of Table III rather heavily underestimate the dissociation energy; the ANO-RCC result shows a considerable improvement over the smaller basis one, passing from 0.78 to 0.97 eV, but is disappointingly in error by about 0.5 eV with respect to the experimental estimate. Again, the situation is not dissimilar from the CIPT2 results of Ref. 22 where the value of 1.07 eV is obtained in the more extended calculation. The CIPT2 method is a hybrid method where the excitations from the active space are treated variationally with MRCI while the others are dealt with perturbationally; an advantage of such a method lies in the removal of the intruder states problem, a disadvantage being, on the other hand, the presence of size consistency errors. In this respect it is worth remarking that the third-order SC-NEVPT approach is completely free from any intruder states problem and is perfectly size consistent. The most striking feature of the SC-NEVPT3 results, though, is the appearance of a second distinct minimum in correspondence with the formation of the 4s-4s bond. In this respect, the results at SC-NEVPT3 level become similar to the findings of the pioneering calculations of Goodgame and Goddard.³² It is remarkable that the high level CIPT2 calculations of Celani *et al.*²² also yield a second minimum, albeit shallower than the one found in the SC-NEVPT3 case. Even though it is likely that the outer minimum of SC-NEVPT3 is too deep, the present calculations, as well as those of Celani *et al.*,²² bring some support for the existence of a secondary 4s-4s minimum in the Cr₂ potential-energy curve.

An analysis of the various contributions which form the third-order result reveals various differential behaviors of the correction functions; partitioning the SC-NEVPT3 energy contribution according to the following scheme:

$$E^{(3)}(S_l^{(k)}) = \sum_{l',k'} \langle \Psi_l^{(k)} | V | \Psi_{l'}^{(k')} \rangle c_l^{(k)} c_{l'}^{(k')}, \quad (6)$$

and collecting all the contributions coming from spaces of the same type, shows that the spaces of type $S_{ij,rs}^{(0)}$ (doubly inactive excitations) and $S_{i,rs}^{(-1)}$ give together a contribution which is positive and roughly constant (≈ 0.015 a.u.) for R

≥ 3.2 a.u. (the location of the inner minimum). The spaces of type $S_{rs}^{(-2)}$, $S_{ij}^{(+2)}$, and $S_{ij,r}^{(+1)}$ all give negative contributions. Altogether such negative contribution shows a small variability, passing from -0.014 a.u. at $R=3.2$ a.u. (inner minimum), to -0.016 a.u. at $R=4.4$ a.u. (maximum), to -0.017 a.u. at $R=5.6$ a.u. (outer minimum), and remaining relatively unchanged afterward.

It is possible that the SC-NEVPT3 calculations suffer, in some measure, from the relatively low number of correction functions that are employed and that better results could be obtained passing on to the PC-NEVPT3 where the whole first-order interacting space is fully taken into account. The implementation of the PC-NEVPT3 will be taken up in future work.

IV. CONCLUSIONS

In this paper the implementation of the third-order NEVPT in its strongly contracted variant has been presented and discussed. The SC-NEVPT3 approach is endowed with the general characteristics of the n -electron valence state PT (Ref. 4) among which the size consistency and the absence of the intruder states problem appear as particularly noteworthy. The importance of having a viable third-order procedure such as SC-NEVPT3 lies, beyond the possible improvement in the description of the system under study, in the possibility of judging on the adequacy of the zero-order wave function; the case of too wide a discrepancy between the second- and third-order results can be a clear indicator that the zero-order description necessitates major improvement. The SC-NEVPT3 approach has been initially tested on two simple cases (CH₂ and N₂) where the third-order contribution brings about a small variation with respect to the second-order results. Furthermore, a remarkably more severe test has been carried out on the potential-energy curve of the chromium dimer using large basis sets; in this case large deviations from the second-order results are introduced by the SC-NEVPT3, clearly revealing the inadequacy of the zero-order description which consists, as usual, of a CASSCF wave function involving the more external electrons and orbitals.

The Cr₂ third-order calculations, though, bear out recent results²² obtained with different high level techniques.

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