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ORIGINAL PAPER

Transition energy and potential energy curves for ionized inner-shell states of CO, O_2 and N_2 calculated by several inner-shell multiconfigurational approaches

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Abstract Potential energy curves and inner-shell ionization energies of carbon monoxide, oxygen and nitrogen molecules were calculated using several forms of the inner-shell multiconfigurational self-consistent field (IS-MCSCF) method—a recently proposed protocol to obtain specifically converged inner-shell states at this level. The particular forms of the IS-MCSCF method designated IS-GVB-PP, IS-FVBL and IS-CASSCF stand for perfect pairing generalized valence bond, full valence bond-like MCSCF and complete active space self consistent field, respectively. A comparison of these different versions of the IS-MCSCF method was carried out for the first time. The results indicate that inner-shell states are described accurately even for the simplest version of the method (IS-GVB-PP). Dynamic correlation was recovered by multireference configuration interaction or multireference perturbation theory. For molecules not having equivalent atoms, all methods led to comparable and accurate transition energies. For molecules with equivalent atoms, the most accurate results were obtained by multireference perturbation theory. Scalar relativistic effects were accounted for using the Douglas-Kroll-Hess Hamiltonian.

Keywords Inner-shell state · Multiconfigurational approach · IS-MCSCF · VB function

Introduction

Inner-shell states have received increasing attention in recent decades. They form the basis of several important experimental techniques such as X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES) spectroscopy, which have benefitted the widespread use of synchrotron radiation. Inner-shell states also represent a challenge for theoretical methods since their description requires proper account of relaxation, correlation and localization effects.

Calculations on inner-shell states are commonly performed at Hartree-Fock (HF) level [1–5], the so-called ΔSCF approach, coupled cluster [6], configuration interaction (CI) based on HF orbitals [7–11], or density functional theory (DFT) [12] Recently, we proposed a method to address the problem at multiconfigurational level [13]. The method was called IS-MCSCF, where IS stands for inner-shell. This approach can circumvent the difficult problem of avoiding the variational collapse of the inner-shell state wave function to the ground state or to the first excited state of a given irreducible representation of the point group of the molecule. The problem of variational collapse in the ΔSCF approach is well discussed [1–5]. In MCSCF level, the variational collapse can sometimes be avoided by choosing a restricted active space, including inner-shell orbital. This active space generates a small number of configurations and the inner-shell state is the highest root of the CI [14, 15]. Jensen et al. [16] proposed an alternative algorithm to avoid variational collapse of the MCSCF wave function. This is a two-step optimization but differs from ours. An intermediate optimization is done with the core orbital kept frozen, which leads the wave function to the local minimum region; a second step consists of a full Newton–Raphson, including the core orbital.

When a molecule presents equivalent atoms, there is an additional problem given that, besides core relaxation, localization of the core hole should be taken into account [17–20]. A former well-designed solution to the problem

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of localization was done as an application of the generalized multistructural function (GMS) of Hollauer and Nascimento [18, 19] to N 1 s transitions in N_2 [20].

We have shown [21] that IS-MCSCF is a suitable method with which to address this problem and basically confirms previous findings [17, 20, 22–26] that the solution of the problem with a localized orbital basis set represents the global minimum, whilst the delocalized solution (symmetry-adapted) represents a local minimum. It was also shown [21] that dynamic correlation can be recovered by means of multireference perturbation theory.

IS-MCSCF and GMS, contrary to the Bagus and Schaefer approach [17], preserves the symmetry of total wave functions in such a way that the full Hamiltonian spectrum is reproduced. IS-MCSCF has the additional advantage of being suitable to describe the whole potential curve and generate a single set of molecular orbitals while still avoiding the problem of nonorthogonality of molecular orbitals present in the GMS approach since in the IS-MCSCF approach both orbitals and CI coefficients are optimized.

In previous works [13, 21], IS-MCSCF was taken essentially as a synonym of IS-CASSCF. It was noted, however, that the method can support any kind of multiconfigurational function. In fact, calculations were reported at HF and two configuration self-consistent field (IS-TCSCF) levels. The use of CASSCF, of course, limits the size of the system in which the method can be applied, and alternative approaches should be tried. In the present work, we present a systematic study of potential curves for inner-shell states calculated at several levels of theory. The first level is perfect-pairing GVB (GVB-PP) [27]. It is well known that GVB-PP functions can be written as multiconfigurational functions in natural orbitals, containing only doubly occupied orbitals [27]. We bring this a step forward by introducing into this multiconfigurational function some configurations corresponding to ionic structures in the VB picture. For this reason we refer to this way of constructing the MCSCF function as full valence-bond-like (FVBL) MCSCF. This function is related to the spin-coupled VB (SCVB) [28] and to the VBSCF [37] methods but with the important difference that these last two work with nonorthogonal orbitals while in the present construction the final orbitals are orthogonal. The last form of MCSCF used in the present work is CASSCF. The number of configurations in GVB-PP and FVBL increases much more slowly that the corresponding number in the CASSCF functions. Dynamic correlation can be recovered by multireference perturbation theory (MRPT), as already mentioned, or by multireference configuration interaction (MRCI), as shown in the present work. The specific states studied are the 1 s ionized states of CO, N_2 and O_2.

The form of MRPT used here is known as general multiconfiguration self-consistent field quasi-degenerate perturbation theory (GMC-QDPT)—a method developed by Nakano et al. [36]. This method allow for more general forms of MCSCF function, not only CASSCF, which is the case studied here. In what follows, MRPT will be used as a synonym of GMC-QDPT.

Theoretical background

Inner-shell states have long been a challenge to theoretical description. A suitable method to treat core-states should account for relaxation of the orbitals as well as correlation correction and, depending on the case, localization of core hole. A natural approach to treat inner-shell states is to make use of methods that describe valence-shell excited states quantitatively. Among them, the combination of MCSCF with perturbation theory or MRCI is particularly prominent. Such progress notwithstanding, a major difficulty with this approach concerns core-shell states: the problem of variational collapse of the excited state to the ground state wave function. Recently [13], we proposed a method to circumvent this problem based on a sequence of constrained optimizations in the orbital mixing step and on restriction of occupation of inner-shell orbitals. Inner-shell and valence-shell orbitals are optimized in different steps, each one corresponding to an SCF cycle. The entire procedure forms a double loop SCF. Briefly, the double loop procedure is composed of two steps. In the first, inner-shell orbitals are optimized for all configurations selected, which depends on the kind of multiconfigurational functions considered. In this step, the other orbitals in the active space are frozen but inner-shell orbitals are allowed to relax. In a second step, the other orbitals are optimized and the core orbitals are kept frozen. The whole procedure is repeated until self-consistency is achieved.

In cases of core equivalent atoms (N_2 and O_2), two solutions are possible. One is based on symmetry-adapted delocalized core orbitals and the other on localized core orbitals.

Transition energies are obtained by subtracting energies calculated independently for ground and inner-shell states. In the present study, we compared results obtained from different forms of MCSCF functions, i.e., GVB-PP, FVBL-MCSCF and CASSCF (perfect pairing generalized valence bond, full valence bond-like MCSCF and complete active space self consistent field, respectively). For each system studied, these functions were constructed in the following way. In carbon monoxide, the electronic configuration for the ground state is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. In order to describe the ground state at GVB-PP, FVBL-MCSCF and CASSCF, the following active space is implied: $(4\sigma)^2(1\pi)^4(6\sigma)^0(2\pi)^0$. This is sufficient to describe the three chemical bonds of the system. Nevertheless, we are interested in the first ionized state at the C 1 s edge. So, we have to include the 2σ (C 1 s) orbital in the active space and restrict it to be occupied by one electron.

This choice for inner and valence shell active space was guided by the fact that this is the minimal space to describe the whole potential curves for the state considered, i.e., $(C1s^{-1})\ ^2\Sigma^+$ .The total number of configurations is 8, 27 and 175 for GVB-PP, FVBL-MCSCF and CASSCF, respectively.

For N_2, the active space was chosen in a similar way, i.e., the valence active space is set up to include three chemical bonds, but in the inner-shell part, we have to include both core-shell orbitals and consequently the number of configurations will be doubled. The N 1 s orbitals have been localized before calculation since we have shown [21] that this represents the solution with lowest energy. The solution with delocalized orbitals is also presented.

For O_2, the active space was composed by oxygen lone pairs, the high spin π orbitals, i.e., those concerning the chemical bond and the inner-shell orbitals. Similarly to the N_2 case, localized and delocalized orbitals were used.

The scalar relativistic contribution to the transition energy is calculated at Douglas-Kroll-Hess [29, 30] method corrected to third order [31].

All calculations were performed with Dunning's aug-cc-pVTZ [38] basis set.

Results and discussion

Carbon monoxide

In the present approach, transition energies are calculated from differences in the energy values of ground and excited states calculated independently at the same level. Table 1 shows the results for the first ionization potential of the C 1 s edge calculated by several methods compared to the experimental value of Medhurst et al. [32]. The final state is designated as $(C1s^{-1})\ ^2\Sigma^+$. As can be seen GVB-PP, FVBL-MCSCF and CASSCF yield similar results, in good agreement with the experimentally recorded transition energy. It is surprising that the simplest wave function, GVB-PP, gave results of a quality similar to the other two. Results obtained at FVBL-MCSCF and CASSCF are identical. It is worth mentioning that these methods lead to transition energies for inner-shell states in quantitative agreement with experimental findings, which is not normally the case for low-lying (valence) states. This kind of agreement was already observed [13].

In order to recover dynamic correlation, two methods can be applied: multireference configuration interaction (MRCI) and multireference perturbation theory (MRPT). These results are also presented in Table 1. It is worth emphasizing that the orbitals that were doubly occupied in the reference function remained doubly occupied in the MRCI calculation. Thus, the recovered dynamic correlation concerns only active electrons in the reference function. The transition energy was not very sensitive to this approach and remained within the same range of values as with the other methods as can be seen in Table 1. An important point to note, however, is that the MRMP approach is much faster (by several orders of magnitude) than MRCI, and takes into account the correlation effects for electrons in doubly occupied orbitals in the reference function.

Scalar relativistic correction can be calculated using the Douglas-Kroll-Hess Hamiltonian [29–31]. Table 1 also shows the previous results with relativistic correction. As can be seen, for C 1 s, correction is small but not negligible. The order of magnitude of relativistic correction agrees with that reported by Rossi and Davidson [2]. Apparently, there can be some cancellations since depending on the method, the relativistic correction augments or diminishes the value of the transition energy.

Figure 1 shows the potential curves for the $(C1s^{-1})\ ^2\Sigma^+$ state calculated by the methods described above without

Table 1 Vertical ionization energy (VIE) for C 1 s edge in carbon monoxide (CO) (eV), calculated at several inner-shell multiconfigurational self-consistent field (IS-MCSCF) levels: generalized valence bond (GVB), full valence bond-like (FVBL) MCSCF (see text) and complete active space self consistent field (CASSCF). For all methods, results considering dynamic correlation by multireference configuration interaction (MRCI) and general multiconfiguration self-consistent field quasi-degenerate perturbation theory (GMC-QDPT) are also shown. Scalar relativistic corrections are calculated by Douglas-Kroll-Hess Hamiltonian

Method	GVB-PP	FVBL	CASSCF	Experimental [32]
VIE	295.91 295.88[a]	295.38 295.52[a]	295.38 295.52[a]	296.13
Method	GVB/MRCI	FVBL/MRCI	CASSCF/MRCI	
VIE	294.46 294.49[a]	295.49 295.63[a]	295.48 295.57[a]	
Method	GVB/GMC-QDPT	FVBL/GMC-QDPT	CASSCF/GMC-QDPT	
VIE	296.31 296.36[a]	295.70 295.66[a]	295.69 295.64 [a]	

[a] Scalar relativistic corrections by Douglas-Kroll-Hess method

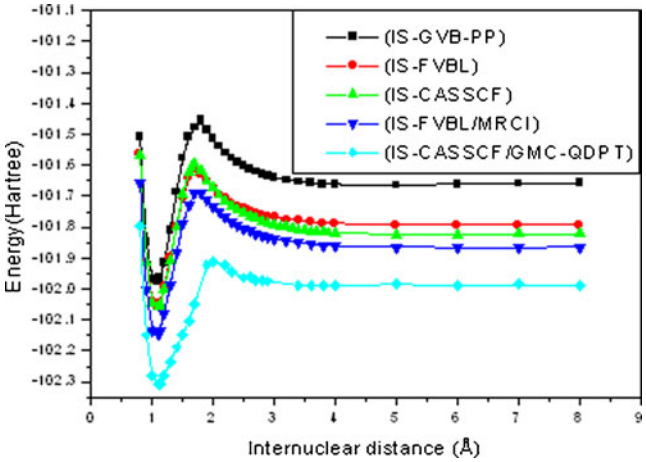

Fig. 1 Potential curves for the (C 1 s^{-1}) $^2\Sigma$ state in carbon monoxide (CO) calculated at several forms of the inner-shell complete active space self consistent field (IS-CASSCF) method and IS-FVBL-MCSCF (inner-shell full valence bond-like–multiconfigurational self-consistent field)-based multireference configuration interaction (MRCI) and CASSCF/GMC-QDPT (general multiconfiguration self-consistent field quasi-degenerate perturbation theory)

relativistic correction. All curves have the same general features. They correspond to a bound state with a bump maximum around 1.75 Å. So, even the simplest method (IS-GVB-PP) is able to describe the curve profile correctly. Absolute values obtained by IS-FVBL-MCSCF and IS-CASSCF methods are quite similar along all curves except the dissociation region. Correlation methods improve the description.

Oxygen

In O_2, a different situation is found since the core-hole left by excitation of the inner-shell electron can rest on each one of the oxygen atoms. The problem of core-equivalent states is well known, and detailed discussions can be found elsewhere [17–26]. One can use a localized or a delocalized (symmetry-adapted) orbital basis set to treat this problem—the former is believed to be the most suitable [17–22].

In previous work with this kind of system [21], we showed that, by choosing a localized description, the IS-CASSCF method leads to underestimation of the transition energy due to the fact that, at this level of calculation, the excited state is better described than the ground state. Table 2 lists the calculated and experimental [33] values of transition energy. As can be seen, all forms of IS-MCSCF on localized basis underestimate the transition energy. MRCI forms do not improve the description when referred to IS-MCSCF methods. This shows that the present construction of the MRCI is not able to recover differential correlation effects. Energy decreases in the same proportion in the ground and excited state, explaining why the transition energy does not change significantly. In reference [21], QMC-QDPT was used to correct the underestimation of the transition energy in the core equivalent system. This has proved to be quite accurate and efficient on computational grounds. We adopted the same procedure here. The result is also shown in Table 2, where a good agreement is finally found. Indeed, the success of this procedure lies in the fact that more dynamic correlation is recovered for the ground than for the excited state. It is

Table 2 VIE for O 1 s edge in O_2 (eV), calculated at several IS-MCSCF levels. IS-SCVB-based MRCI and several forms of IS-MCSCF-based MRPT. Results for localized and delocalized orbital basis set are shown. Scalar relativistic correction are calculated by Douglas-Kroll-Hess Hamiltonian

Method	GVB-PP	FVBL	CASSCF	Experimental [33]
VIE localized basis	532.46	532.04	532.35	543.37
	532.76[a]	532.33[a]	532.64[a]	
VIE delocalized basis	541.83	547.90	544.01	
	542.17[a]	548.24[a]	544.31[a]	
Method	GVB/MRCI	FVBL/MRCI	CASSCF/MRCI	
VIE localized basis	532.84	531.96	532.65	
	—[b]	532.25[a]	533.35	
VIE delocalized basis	541.61	546.87	543.36	
	541.89[a]	547.20[a]	543.78[a]	
Method	GVB/GMC-QDPT	FVBL/GMC-QDPT	CASSCF/GMC-QDPT	
VIE localized basis	545.41	544.60	544.35	
	545.75[a]	545.20[a]	544.64[a]	
VIE delocalized basis	544.06	541.06	542.69	
	544.49[a]	541.30[a]	542.87[a]	

[a] Scalar relativistic corrections by Douglas-Kroll-Hess method.

[b] Not reported due to convergence problems.

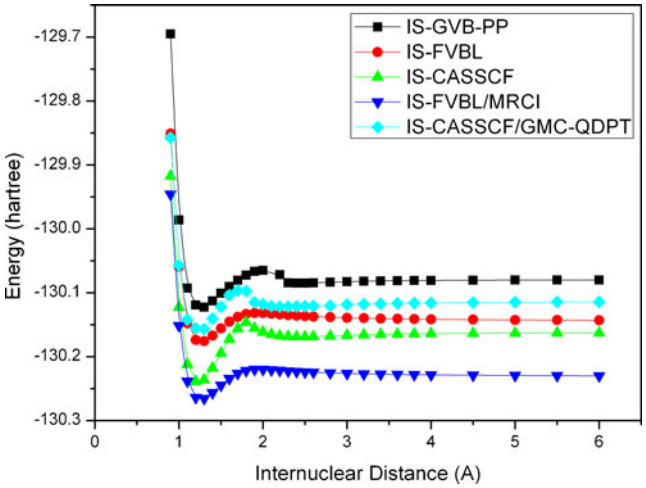

Fig. 2 Potential curves for the (O 1 s^{-1}) $^4\Sigma_u$ state in O_2 calculated at several forms of the IS-CASSCF method and IS-FVBL-MCSCF-based MRCI and CASSCF/GMC-QDPT

worth emphasizing that all orbitals doubly occupied in the MCSCF reference were included in MRPT, explaining why this method recovers more correlation energy than the MRCI indicated above.

Table 2 also presents results for the calculation of transition with delocalized (symmetry-adapted) orbital basis. These are in reasonably good agreement with experimental values for IS-CASSCF. Agreement is better than that observed before for pre-ionization-edge states [21].

This result apparently contradicts the prediction of Bagus and Schaefer [17] that the delocalized basis leads to a result of more than 10 eV above the experimental value. The difference can be rationalized, however, Bagus and Schaefer's result was obtained at HF level and our calculation is multiconfigurational. The latter better takes into account relaxation as well as part of the correlation. The wave function is more flexible and has a greater number of variational parameters. In fact, we have shown [21] for N_2 that the transition energies for the states (N 1 s^{-1} π_g^*) $^1\Pi_{g,u}$, decrease from 410 to 404 eV when going from HF to CASSCF with a delocalized basis set, the latter being close to the experimental value of 401 eV. So, what is going on here is a compensating effect due to inadequacy of the delocalized basis (non-dynamic correlation). In fact, it has long been shown that improvement over delocalized description can be achieved by high-correlated methods [34]. In the case of O_2, IS-MCSCF in delocalized basis performs better for the (O1s^{-1}) $^4\Sigma_u$ state than it did for the above-mentioned N 1 s states. This could be related to the fact that the state is an ionized state and that relaxation due to the resulting charge is relatively more important than the case of neutral final states. For IS-GVB-PP and IS-FVBL-MCSCF, the agreement is poorer and the deviations are not in the same direction, the former underestimates and the latter overestimates the value. The corresponding transition energies lie around the same value on the localized basis. So, IS-MCSCF on delocalized basis can improve the corresponding results on HF level, although the good agreement with experiment could be fortuitous.

In any case, concerning the present approach, results for localized and delocalized orbitals basis set converge to experimental values when treated at MRPT level. This has

Table 3 VIE for N 1 s edge in N_2 (eV), calculated at several IS-MCSCF levels. IS-SCVB-based MRCI and several forms of IS-MCSCF-based MRPT. Results for localized and delocalized orbital basis set are shown. Scalar relativistic correction are calculated by Douglas-Kroll-Hess Hamiltonian

Method	GVB-PP	FVBL	CASSCF	Experimental [35]
VIE localized basis	403.39	402.95	402.96	409.9
	402.15[a]	403.10[a]	403.11[a]	
VIE delocalized basis	409.33	410.54	410.68	
	410.42[a]	410.76[a]	410.76[a]	
Method	GVB/MRCI	FVBL/MRCI	CASSCF/MRCI	
VIE localized basis	403.02	403.00	404.12	
	401.91[a]	402.94[a]	—[b]	
VIE delocalized basis	408.92	410.10	410.10	
	—[b]	410.10[a]	410.28[a]	
Method	GVB/GMC-QDPT	FVBL/GMC-QDPT	CASSCF/GMC-QDPT	
VIE localized basis	410.45	410.36	410.36	
	409.61[a]	410.60[a]	410.62[a]	
VIE delocalized basis	410.10	409.71	409.38	
	410.10[a]	410.23[a]	409.49[a]	

[a] Scalar relativistic corrections by Douglas-Kroll-Hess method

[b] Not reported due to convergence problems

already been observed [21]. It is important to emphasize that in both cases (localized and delocalized orbitals) the final wave function has the full symmetry of the Hamiltonian.

In our approach, localization is performed as in GMS but, different from the latter method, orbitals as well as CI coefficients are allowed to vary. In the end, one has only one set of localized orbitals but the total wave function has the full symmetry of the Hamiltonian as already stated.

As expected, relativistic corrections for O 1 s edge are slightly more significant than those of C 1 s and once more their order of magnitude is compatible with that reported by Rossi and Davidson [2].

In Fig. 2, one can find potential energy curves for the $(O1s^{-1})\ ^4\Sigma_u$ state of O_2 for several methods on a localized basis and without relativistic correction. The bump maximum lies at 2.0 Å and 1.8 Å for IS-GVB and IS-CASSCF, respectively. For IS- FVBL-MCSCF and IS-FVBL-MCSCF/MRCI, it is flatter and lies at 1.9 Å. It can be observed in Fig. 2 that for the non-variational method IS-CASSCF/GMC-QDPT the energy lies above that of the corresponding IS-CASSCF function in the localized basis. Transition energy agrees well with experimental results, as shown in Table 2.

Nitrogen

In N_2, the situation is quite similar to that of the O_2 molecule. Results are shown in Table 3 and compared to the experimentally determined ionization potential [35]. Once more, all forms of IS-MCSCF lead to an underestimation of the transition energy on a localized basis. It is worth mentioning that the IS-CASSCF results presented here differ from that presented in reference [21] due to the fact that the latter result was obtained by state averaging the density of the $(N\ 1\ s^{-1})\ ^2\Sigma_u$ and $(N\ 1\ s^{-1})\ ^2\Sigma_g$ states, while in the present work only the first of these was used in the optimization. Yet again, the IS-FVBL-MCSCF/MRCI was unable to improve the result when referring to all forms of IS-MCSCF but IS-GMC-QDPT leads to results in good agreement with experimental findings.

As in the case of O_2, on a delocalized basis the results show surprisingly good agreement with the experimental value, for reasons discussed above in the context of O 1 s edge. Relativistic corrections are also shown and are of the same order of magnitude as in previous cases.

Figure 3 shows the potential curves for $(N\ 1\ s^{-1})\ ^2\Sigma_u$, calculated at several IS-MCSCF levels on a localized basis and without relativistic correction. All curves have the same profile. Contrary to what happens in the O_2 case, in Fig. 3 the energy obtained at IS-CASSCF/GMC-QDPT level lies slightly below that of the corresponding IS-CASSCF function in the localized basis. In spite of this, the transition energy agrees well with experimental results also in the case of N_2, as can be seen in Table 3.

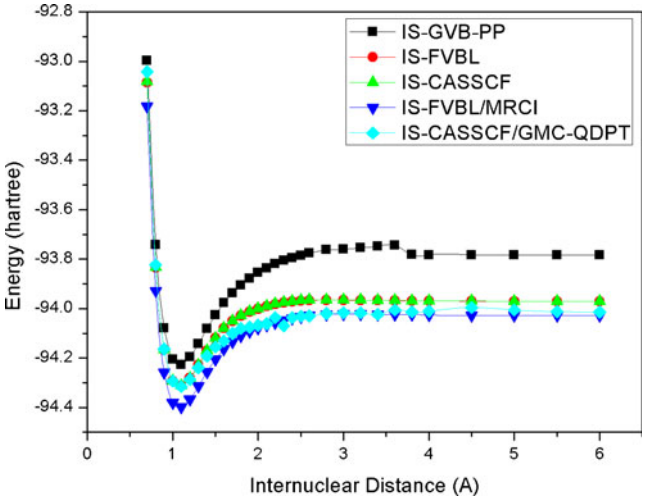

Fig. 3 Potential curves for the $(N\ 1\ s^{-1})\ ^2\Sigma_u$ state in N_2 calculated with several forms of the IS-CASSCF method and IS-FVBL-MCSCF-based MRCI and CASSCF/GMC-QDPT

Conclusions

We have investigated the performance of several forms of IS-MCSCF wave functions, namely IS-GVB-PP, IS- FVBL-MCSCF and IS-CASSCF, in calculation of the ionization potential of C 1 s edge in CO, O 1 s edge in O_2 and N 1 s edge in N_2. Transition energy and potential energy curves show that all forms of the IS-MCSCF function lead to a good description of the inner-shell state. Quantitative results were obtained at these levels for molecules not containing equivalent atoms. This was exemplified with CO. For molecules with equivalent atoms (O_2 and N_2), the method underestimates the transition energy if a localized orbital basis set is used, given that the excited state is better described at this level than the ground state. MRCI, in the form presented here, did not succeed in improving the results derived from IS-MCSCF approaches. Quantitative agreement could be obtained for O_2 and N_2 inner-shell transitions by using MRPT. Results were equivalent in all forms tested here, i.e., IS-GVB-PP/GMC-QDPT, IS-FVBL-MCSCF/GMC-QDPT and IS-CASSCF/GMC-QDPT. The most important conclusion is that the simplest form of the theory, IS-GVB-PP or IS-GVB-PP/GMC-QDPT can lead to quantitative agreement with experimental core-shell ionization potential. This has not been verified in valence transitions in essentially any form of multiconfigurational function, not even CASSCF.

The binding energies for N_2 and O_2 calculated by all forms of IS-MCSCF in the delocalized description presented better agreement with experimental values than the corresponding localized values. This raises the question, which description is best? If one naively takes only agreement with experiment into account the delocalized would be considered the best. This is misleading, since the value of

the total energy is lower in the localized description. The reason for the underestimation of the transition energy in the localized picture is clear. The excited state is better described than the ground state at this level. The agreement in the delocalized picture seems to be fortuitous. It is important to emphasize though, that both localized and delocalized pictures lead to equivalent results when the calculation is performed at IS-GMC-QDPT level.

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