Generalized multistructural calculation of the optical and generalized oscillator strengths for inner-shell excitations in N_2

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The effect of orbital relaxation, hole localization, and electron correlation on the transition energy, optical oscillator strength (OOS), and generalized oscillator strength (GOS) for the $(1\sigma_u \to 1\pi_g, 1\sigma_g \to 1\pi_g)$ process in nitrogen has been examined using the generalized multistructural (GMS) wave function. It is shown that the transition energy is largely affected by hole localization while for the GOS and OOS orbital relaxation effects dominate. The behavior of the GOS as a function of the transferred momentum is very well described by the GMS wave function, in the first Born approximation, for small and medium values of the transferred momentum k^2.

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I. INTRODUCTION

In the past few years much work has been devoted to the study of inner-shell excitations of molecules by photons and electrons. An extensive and up to date bibliography on this subject was collected by Hitchcock [1].

In particular, the strong excitation process $(1\sigma_u \to 1\pi_g, 1\sigma_g \to 1\pi_g)$ in the N_2 molecule, sometimes referred as preionization peak, has been examined both experimentally and theoretically. On the experimental side, optical [2–8] oscillator strengths have been determined by different techniques and generalized oscillator strength by Camilloni et al. [7] and very recently by Barbieri and Bonham [8]. Theoretical values for the optical oscillator strength (OOS) have been calculated by several authors [9–16] and for the generalized oscillator strength (GOS) by Rescigno and Orel [12].

When an inner-shell electron is promoted to a valence-like orbital several important structural changes occur. Orbital relaxation is one of them and in order to properly take into account this effect on the GOS and OOS values, nonorthogonal target wave functions should be used. In the past some attempts have been made in order to describe indirectly these effects by a configuration interaction (CI) calculation, using the same set of orthogonal orbitals to represent both the ground and the excited states. It was recently shown [17] that this procedure (CI with single excitations from all occupied orbitals to all the virtual space) correctly reproduces relaxation effects in GOS calculations for valence excitations. However, for inner-shell excitations this procedure is not very effective because the inner-shell excited state, being at a much higher energy than the valence ones of the same symmetry, would only appear as a high root in the CI calculation.

Another important aspect to be considered when an inner-shell electron is excited in molecules like N_2 is the description of the hole produced in this process. As discussed by Rescigno and Orel [12], it is necessary to determine the target excited-state wave function in the presence of the localized hole in order to reproduce the excitation energy. Those authors [12] also showed that the OOS and GOS values are very sensitive to the target description. They [12] have tried to include this effect, but did not consider the full symmetry of the molecule because, in order to localize the hole, a lower symmetry was used. The problem of symmetry breaking in this and other similar processes has been discussed by several authors [18–21].

In the present work optical oscillator strengths and generalized oscillator strengths [within the first Born approximation (FBA)] have been calculated taking relaxation effects directly into account by using wave functions constructed from molecular orbitals optimized for each of the states involved in the transition.

The problem of recovering the full molecular symmetry was accomplished by the use of a generalized multistructural wave function [22–24], which is particularly suitable to treat situations where the description of the molecular state requires localized solutions. This wave function also provides a very convenient way of treating the electron correlation problem, avoiding large CI expansions. This procedure allowed us to calculate the contribution of the different effects (orbital relaxation, hole localization, and electron correlation) to the excitation energies, OOS and GOS values, as will be discussed in the following section.

Previous attempts to estimate these contributions have used pure theoretical arguments [18] or orthogonal CI calculations [12]. However, as will be shown, we found qualitative [12,18] , but not quantitative [12], agreement between their predictions and the results of our calculations.

II. COMPUTATIONAL DETAILS

The calculations of the GOS in the FBA were performed using both Hartree-Fock (HF) and generalized multistructural (GMS) wave functions [22–24] expanded on a basis of Gaussian-type orbitals. The $[9s, 5p, 1d]$ basis presented previously [17,25] was partially uncontracted to allow a better description of the relaxation process following the electron excitation, mainly in the inner-shell molecular region, giving rise to the $(13s, 7p, 1d)/[10s, 6p, 1d]$ basis set used in the present calculation.

Only a brief description of the GMS wave function will be presented here. A full discussion of the theory, with a detailed description of all the computational aspects involved in obtaining the solution of this kind of wave function, can be found elsewhere [22–24].

A GMS wave function can be defined as

$$\psi_{GMS} = \sum_{I=1}^{N_{struct}} \sum_{i=1}^{N_{sef}} c_i^I \varphi_i^I , \tag{1}$$

where φ_i^I represents the ith spin-eigenfunction (N_{sef}) of the Ith bonding structure (N_{struct}) and c_i^I its weight in expansion (1). In principle, there are no restrictions whatsoever on the form of the wave function φ_i^I. Each of the φ_i^I's can be individually optimized at the HF or multiconfigurational (generalized valence-band method, complete-active-space self-consistent-field method, etc.) level, followed or not by a CI treatment, or else can be taken simply as a VB-type function. In this last case the ψ_{GMS} is obviously identical to the VB function of the molecule.

Each one of the φ_i^I is represented in a basis of orthogonal orbitals $\{\phi_\alpha^I\}$, properly optimized for the Ith structure. Although the orbitals of a given structure are taken to be orthogonal to each other,

$$\langle \phi_\alpha^I | \phi_\beta^I \rangle = \delta_{\alpha,\beta} , \tag{2}$$

no such restriction exists for the orbitals belonging to different structures I and II,

$$\langle \phi_\alpha^I | \phi_\beta^{II} \rangle = S_{\alpha,\beta}^{I,II} . \tag{3}$$

The coefficients c_i^I are obtained variationally by solving the equations

$$\langle \delta\psi_{GMS} | H - E | \psi_{GMS} \rangle = 0 , \tag{4}$$

$$(H - SE)C = 0 , \tag{5}$$

where H and S are interaction supermatrices containing the diagonal (same structure) and the interstructural matrix elements. The matrix elements involving orbitals belonging to different structures are computed using a biorthogonalization procedure and for this purpose a new computer code was developed.

Figure 1 shows the structures used in the present calculations and also schematically the way the GMS wave function was constructed. As depicted in Fig. 1, HF wave functions are constructed exhibiting holes localized [22] on the left and on the right nitrogen atom, which are then recombined to recover the full symmetry of the mol-
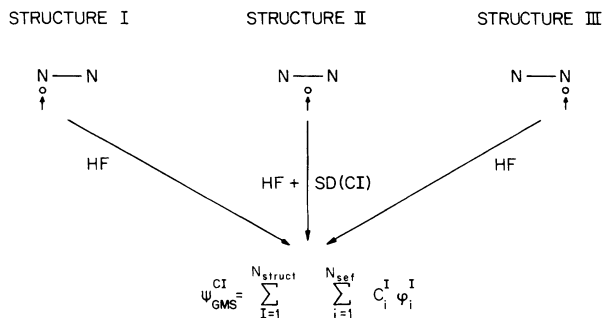

FIG. 1. The generalized multistructural wave functions for the N_2 molecule: GMS-2S is the superposition of the HF wave function for structures I and III, while the GMS-3S includes structure III as well. The GMSCI includes SD excitations from the HF reference configuration of structure II.

ecule. The delocalized structure is also considered in order to allow complete flexibility to the wave function. The coefficients c_i^I will then determine the degree of localization (or delocalization) of the hole state.

In order to discuss the influence of each of the different effects involved in the target description when a core electron is excited (i.e., relaxation, hole localization and electron correlation) five different wave functions were calculated and from those, both the OOS and GOS were computed. The different wave functions used resulted from the following calculations:

(1) A Hartree-Fock calculation in which the molecular orbitals (MO's) optimized for the ground state of the molecule are also used for the excited state. In this case none of the above mentioned effects are included. We shall call this the Hartree-Fock frozen-core calculation (HFFC).

(2) A Hartree-Fock calculation with the MO's for the ground and excited states being independently optimized. In this calculation, orbital relaxation effects are directly included. We shall call this the Hartree-Fock relaxed calculation (HFR).

(3) A GMS calculation with two nonorthogonal sets of molecular orbitals for the excited state, one optimized in the presence of the $1s$ hole on the left nitrogen atom $N(L)$, and the other describing the hole on the right nitrogen atom, $N(R)$. Only two configurations are used in this GMS wave function, one corresponding to a hole localized on the left atom and the particle in the π_g MO, and the other describing the hole localized on the right atom with the particle in the π_g MO. We shall call this a GMS-2 structure wave function (GMS-2S). This calculation includes not only relaxation effects (which were already included in the HFR calculation), but also localization effects and relaxation in the presence of localized hole.

(4) A GMS calculation using three nonorthogonal sets of molecular orbitals for the excited state, the same two sets used in the GMS-2S and the one used in the HFR calculation. Each set of configurations corresponds to one of the structures shown in Fig. 1, i.e., one with the

hole localized in the left atom and the particle in the π_g MO, the one obtained by reflection of the previous structure, and the third one associated with the structure with a delocalized hole and the particle in the π_g molecular orbital. We shall call this a GMS-3 structure wave function (GMS-3S). This calculation differs from the GMS-2S one because now the molecule can choose (in the variational sense) how much localized or delocalized the hole is, once we are mixing configurations built up from localized and delocalized MO's.

(5) A GMS calculation including the same three sets of MO's used in the GMS-3S wave function plus several other configurations, related to inner-shell and valence correlations and we shall call this a GMSCI wave function. In this case we include some selected configurations related to single and double (SD) excitations from all the occupied orbitals to a virtual space formed with 18 improved virtual orbitals [26] of σ_g, σ_u, π_g, and π_u symmetries, determined from the HFR calculation. The configurations were selected as those which contributed to an energy lowering of 5×10^{-5} in a CI(SD) calculation using the orthogonal orbitals of structure II. We believe that this GMSCI wave function, besides recovering the full symmetry of the molecule, incorporates all the important effects necessary to describe the excited state of the N_2 molecule when an inner-shell electron is excited, namely orbital relaxation, hole localization, and correlation effects.

In the determination of the excitation energy, OOS and GOS, for calculations (1)–(4) (HFFC, HFR, GMS-2S, and GMS-3S), a HF reference wave function was used for the ground state. For the GMSCI case, the ground state was also represented by a CI wave function with the configurations selected by a procedure similar to the one used to construct the GMSCI wave function.

To determine the OOS and GOS at the different levels of calculation, a new computer code was written which incorporates a biorthogonalization procedure allowing matrix elements between nonorthogonal orbitals to be computed.

III. RESULTS AND DISCUSSIONS

A. Excitation energy

Table I presents the values for the excitation energy obtained at the different levels of calculations for the two processes considered. The experimental result for the vertical excitation energy of the unresolved peak is 401.1 eV [27].

Comparing the results from the different calculations presented in Table I one can observe the influence of the different effects on the excitation energy (ΔE).

Relaxation effects. The comparison between the results of calculation (1), in which the frozen-core approximation was used, and calculation (2), in which the orbitals were allowed to relax fully, should give a good estimate of the importance of relaxation effects to the transition energy. From Table I one sees that this effect amounts to approximately 3 eV. It is important to emphasize that only structure II (Fig. 1), which describes a delocalized hole,

TABLE I. Transition energies at different levels of calculation.

Target wave function	excitation energy (eV)	
	$1\sigma_u \rightarrow 1\pi_g$	$1\sigma_g \rightarrow 1\pi_g$
(1) HFFC	413.64	413.70
(2) HFR	410.56	410.65
(3) GMS-2S	401.13	401.20
(4) GMS-3S	400.95	401.02
(5) GMSCI	402.55	402.62

has been used in calculations (2). Therefore, at this point, the relaxation effect associated to the hole localization has not yet been computed.

Hole localization. Relaxation effects associated to the hole localization can be inferred from the results of calculations (2) (HFR) and (3) (GMS-2S). In both calculations all the orbitals are allowed to relax fully [28], the main difference being that in calculation (3) the orbitals are optimized in the presence of a localized hole. Therefore the difference in the transition energies computed at these levels of calculation ($\Delta E_3 - \Delta E_2$) should reflect the importance of the hole localization. From Table I it is clear that hole localization is by far the most important effect, being responsible for a decrease of 9.4 eV in the transition energy relative to the delocalized hole picture.

Degree of hole localization. The difference in the transition energies obtained from calculations (3) (GMS-2S) and (4) (GMS-3S), $\Delta E_4 - \Delta E_3$, can be related to the degree of hole localization inasmuch as the GMS-3S wave function allows the mixing of both descriptions to be variationally determined. As seen from Table I, this effect on the transition energy is small (0.2 eV), which is an indication that the delocalized structure (II) contributes very little to the description of the excited state. This is confirmed by the analysis of the wave function which shows that structure II contributes with a small coefficient (c^{II}) to the GMS-3S expansion. The hole state is therefore preferably localized.

Correlation effects. Correlation effects have been considered in calculation (5), by adding to the GMS-3S expansion singly and doubly excited configurations from the HF wave function of structure II, as described above. The results shown in Table I are consistent with the fact that at this level of treatment the ground state is generally favored. Transition energies equivalent to the ones from calculations (3) and (4) could be obtained if higher excitations were included in the CI expansion. However, due to the nonorthogonality of some of the orbitals, and considering our present computational facilities, a larger CI calculation would be unpractical.

B. Optical oscillator strength

The values for the OOS calculated at the different levels are presented in Table II together with other available experimental and theoretical results. Several interesting conclusions can be drawn from the comparison of the OOS values calculated with the different target wave

TABLE II. The absolute optical oscillator strengths at different levels of calculation compared to the experiments and other theoretical results.

	OOS	Technique
Experimental		
Wuilleumier and Krause [2]	0.12	Optical absorption
Kay, van der Leeuw and van der Wiel [4]	0.20	Electron-energy loss
Bianconi et al. [3]	0.23	Optical absorption
Oda, Nishimura, and Osawa [5]	0.14	Electron-energy loss
Zhadenov, Akimov, and Vinogradov	0.21	Optical absorption
Camilloni et al. [7]	0.20	Electron-energy loss
Barbieri and Bonham [8]	0.18	Electron-energy loss
Theory		
(i) This work		
(1) HFFC	0.26	
(2) HFR	0.21	
(3) GMS-2S	0.19	
(4) GMS-3S	0.18	
(5) GMSCI	0.20	
(ii) Other theoretical results		
Dehmer and Dill [9]	0.23	
Rescigno and Langhoff [10]	0.26	
Iwata, Kosugi, and Nomura [11]	0.37	
Rescigno and Orel [12]	0.12	
Arneberg et al. [13]	0.13	
Rescigno and Orel [14]	0.24	
Cosman and Wallace [15]	0.11	
Barth and Schimer [16]	0.20	

functions. From the results of Table II it is clear that the OOS value is most affected by the relaxation of the molecular orbitals. The OOS value of 0.261 obtained with the HFFC wave function drops to 0.207 when the molecular orbitals are allowed to relax. The other effects do change the OOS value a little, but not as much as the MO's relaxation. Another interesting observation is that hole localization lowers the calculated OOS value [compare the results of calculations (2) and (3)], while correlation effects raise the OOS value [compare the results of calculations (4) and (5)]. Nevertheless, the net effect is very small as can be seen from the comparison of calculations (2) and (5).

There is considerable disagreement among the experimental data shown in Table II. However, our OOS value obtained at the highest level of calculation (GMSCI) supports the experimental results of Kay, van der Leeuw, and van der Weil [4] Camilloni et al. [7], and presents a reasonable agreeement with the results of Zhadenov, Akimov, and Vinogradov [6] and Barbieri and Bonham [8].

There is also considerable disagreement among the several theoretical results previously reported in the literature (see Table II) and it would be instructive to analyze them in the light of our results obtained at the different levels of calculation.

In the calculation of Rescigno and Langhoff [10] the frozen-core approximation was used and a value of 0.26 for the OOS was obtained in perfect agreement with the results of our equivalent calculation (1).

The calculation of Rescigno and Orel [14] tries in a

very interesting way to simulate the relaxation and localization effects with an orthogonal CI calculation. Unfortunately, this procedure presents some problems. First, the wave function for the excited state is not an eigenfunction of the molecular symmetry operators. Second, the calculated value of 0.24 for the OOS seems to include only partially these effects. This can be seen comparing their result with our value of 0.19 obtained at the GMS-2S level, where orbital relaxation and hole localization are directly included.

The value of 0.13 obtained by Arnenberg et al. [13] is difficult to understand on the basis of our calculations. Since the authors claim that the molecular orbitals were independently optimized, for the ground and excited states, and that hole localization and correlation effects have been included, one should expect a value close to 0.20 for the OOS, in agreement with the results of the GMSCI calculation. The reason for this large discrepancy could be attributed to an over contraction of their basis set [13], in the inner-shell region, to the process of selecting the configurations for the computation of the OOS or else to the combination of both factors.

Dehmer and Dill [9], employing the multiple scattering (MS $X\alpha$) method with a muffin-tin potential, obtained a value of 0.23 for the OOS. Their methodology differs substantially from ours, which makes impossible a comparative analysis in terms of relaxation and correlation effects. The multiple-scattering method was also employed by Kosman and Wallace [15], but in this case a much lower value for the OOS (0.108) was found (this

value was estimated by Zhadenov, Akimov, and Vinogradov [6] from the graphic representation of the result of Kosman and Wallace [15]). The reasons for the discrepancy in the values obtained by the MS $X\alpha$ method [9,15] are not clear.

Finally Barth and Schirmer [16], using the second-order algebraic diagrammatic construction (ADC-2) to the polarization propagator, obtained a value of 0.20 for the OOS, in agreement with our GMSCI value. However, their calculation is not strictly equivalent to the GMSCI. Orbital relaxation was only indirectly considered through particle-hole (p-h), excitations with respect to a HF ground state and although correlation effects were included in the description of both the initial and final states, hole localization has not been considered. Also a substantial reduction of the ADC(2) configuration space was achieved by decoupling core-level excitations from valence-level excitations. The effect of this core-valence approximation on the transition energies was found [16] to be typically of the order of 1 eV, but no such analysis was presented for the oscillator strengths. It is possible that the observed equality of the OOS values obtained from the two nonequivalent calculations [GMSCI and ADC(2)] results from the use of the core-valence approximation in the ADC(2) description.

C. Generalized oscillator strength

Figure 2 presents the calculated GOS results for the dipole-forbidden $1\sigma_g \rightarrow 1\pi_g$ excitation process and Fig. 3 for the dipole-allowed $1\sigma_u \rightarrow 1\pi_g$ process at the different levels of calculation. One observes that also for this property it is the inclusion of relaxation effects that causes the largest variation in the GOS values compared to the HFFC results. Once more localization and correlation effects contribute in opposite directions, and the net effect is again small. As a consequence, as can be seen from Figs. 2 and 3, the results obtained at the GMS-2S and
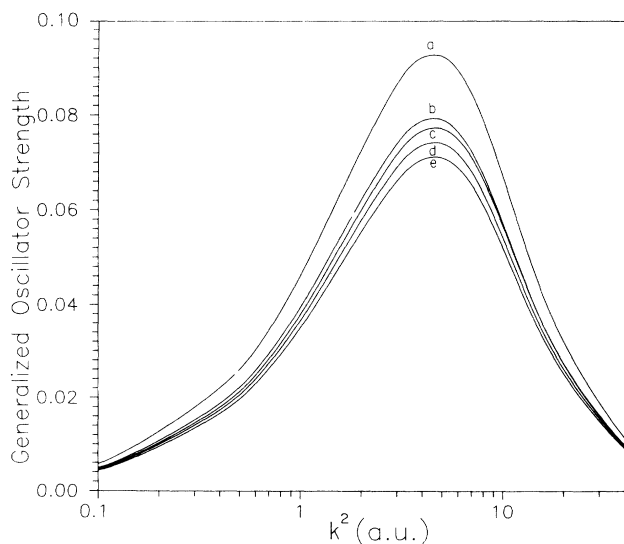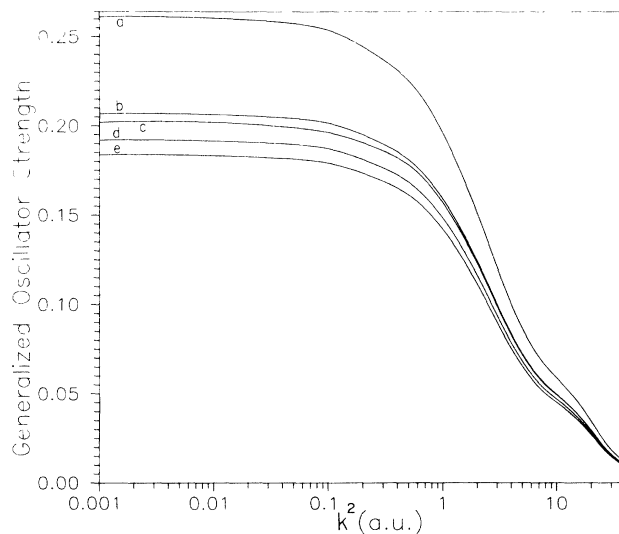
FIG. 3. The generalized oscillator strength for the $1\sigma_u \rightarrow 1\pi_g$ transition at different levels of calculation: (a) HFFC, (b) HFR, (c) GMSCI, (d) GMS-2S, (e) GMS-3S.

GMS-3S levels do not differ appreciably from the ones of the GMSCI calculation.

It is interesting to compare our calculated values with the experiments [7,8] and the results of Rescigno and Orel. Since experimentally the two levels are unresolved, we have to add the calculated GOS values for the two transitions in order to compare the theoretical results with the experiments. The calculated values for this sum, obtained at the HFFC and GMSCI levels of calculation, together with the other experimental [7,8] and theoretical [14] results are shown in Fig. 4.

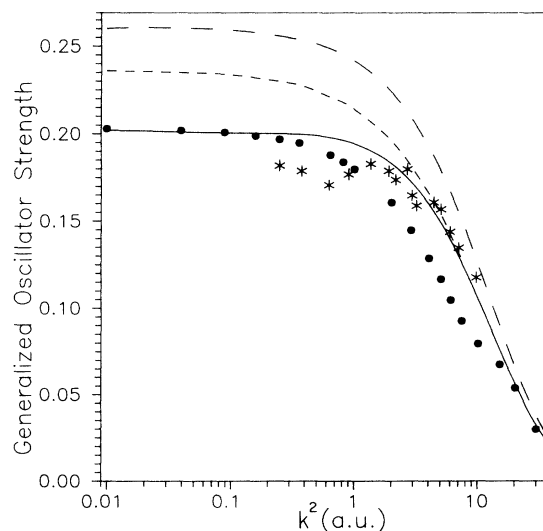From the figure one observes that the GOS calculated by Recigno and Orel [14] falls between our HFFC and

FIG. 2. The generalized oscillator strength for the $1\sigma_g \rightarrow 1\pi_g$ transition at different levels of calculation: (a) HFFC, (b) HFR, (c) GMSCI, (d) GMS-2S, (e) GMS-3S.

FIG. 4. Total generalized oscillator strength for the preionization peak compared to the experiments and other theoretical results: ——— GMSCI; — — —, HFFC; – – –, Rescigno and Orel [14]; ●, expt. of Camilloni et al. [7]; *, expt. of Barbieri and Bonham [8].

GMSCI results. This is an expected result as they tried to reproduce the relaxation and localization effects using an orthogonal CI. Also for the GOS values, as in the previously discussed OOS values, they only partially reproduce these effects in their calculations.

Very good agreement is observed between our GOS values and the results of Camilloni et al. [7] for small K^2 values and with the recent results of Barbieri and Bonham [8] for larger values of K^2. For larger values of K^2, which correspond to larger scattering angles, the experimental results of Camilloni et al. [7] and the results of Barbieri and Bonham [8] disagree within each other. Our theoretical values support the result of Barbieri and Bonham [8] in this K^2 region. It should be emphasized, however, that the FBA could make incorrect predictions for larger scattering angles, a situation that has been observed before [17,25,29,30] for valence and inner-valence excitation processes. Therefore higher-order corrections to the first Born approximation might be necessary in order to describe properly the collision process for larger scattering angles.

IV. CONCLUSIONS

The GMS wave function has proven to be an useful tool to examine the effects of orbital relaxation, hole localization, and electron correlation associated with inner-shell excitation processes. By allowing those effects to be explicitly included in a step-by-step procedure, the GMS wave function provides a clear picture of the influence of orbital relaxation, hole localization, and electron correlation on the transition energy, OOS and GOS values for the preionization process in nitrogen.

The transition energy is largely affected by hole localization, while for the GOS and OOS orbital relaxation dominates. Also, the behavior of the GOS as a function of the transferred momentum, for small and medium values of K^2, is well described by the GMS wave function, within the first Born approximation.

[1] A. P. Hitchcock, Bibliography on Atomic and Molecular Inner-Shell Excitation Studies, updated to 1990 from A. P. Hitchcock, J. Electron Spectrosc. 25, 245 (1985).

[2] F. Wuilleumier and M. O. Krause (unpublished).

[3] A. Bianconi, H. Petersen, F. C. Brown, and R. A. Bacharach, Phys Rev. A 17, 1907 (1978).

[4] R. B. Kay, Ph.E. van der Leeuw, and M. J. van de Wiel, J. Phys. B 10, 2513 (1977).

[5] N. Oda, T. Nishimura, and T. Osawa, in Abstracts of Contributed Papers, XI International Conference on the Physics of Electronic and Atomic Collisions, Kyoto, 1979, edited by K. Tatayangi and N. Oda (North-Holland, Amsterdam, 1979), p. 408.

[6] A. V. Zhadenov, V. N. Akimov, and A. S. Vinogradov, Opt. Spektrosk. 62, 340 (1987) [Opt. Spectroc. (USSR) 62, 204 (1987)].

[7] (a) R. Camilloni, E. Fainelli, G. Petrocelli, and G. Stefani, J. Phys. B 20, 1839 (1987); (b) R. Camilloni, E. Fainelli, G. Petrocelli, G. Stefani, F. Maracci, and R. Platania, in Wavefunctions and Mechanisms for Electron Scattering Processes, edited by F. A. Gianturco and G. Stefani, Lecture Notes in Chemistry Vol. 35 (Springer, Berlin, 1984), p. 172.

[8] R. S. Barbieri and R. Bonham (unpublished).

[9] J. L. Dehmer and D. Dill, J. Chem. Phys. 65, 5327 (1976).

[10] T. N. Rescigno and P. W. Langhoff, Chem. Phys. Lett. 51, 65 (1977).

[11] S. Iwata, N. Kosugi, and O. Nomura, Jpn. J. Appl. Phys. 17, 105 (1978).

[12] T. N. Rescigno and A. E. Orel, J. Chem. Phys. 70, 3390 (1979).

[13] R. Arneberg, H. Ågren, J. Müller, and R. Manne, Chem. Phys. Lett. 91, 362 (1982).

[14] T. N. Rescigno and A. E. Orel, in Wavefunctions and Mechanisms for Electron Scattering Processes [Ref. [7(b)]], p. 215.

[15] W. M. Kosman and S. Wallace, J. Chem. Phys. 82, 1385 (1985).

[16] A. Barth and J. Schirmer, J. Phys. B 18, 867 (1985).

[17] C. E. Bielschowsky, M. A. C. Nascimento, and E. Hollauer, Phys. Rev. A 42, 5223 (1990).

[18] L. S. Cederbaum and W. Domcke, J. Chem. Phys. 66, 6086 (1977).

[19] Y. Ma, F. Sette, G. Meigs, S. Modesti, and C. T. Chen, Phys. Rev. Lett. 19, 2044 (1989).

[20] Y. Ma, F. Sette, G. Meigs, S. Modesti, and C. T. Chen, Phys. Scr. 41, 833 (1990).

[21] F. X. Gadea, H. Köppel, J. Schirmer, L. S. Cederbaum, K. J. Randall, A. M. Bradshaw, Y. Ma, F. Sette, and C. T. Chen, Phys. Rev. Lett. 66, 883 (1991).

[22] E. Hollauer and M. A. C. Nascimento, Chem. Phys. Lett. 184, 470 (1991).

[23] E. Hollauer and M. A. C. Nascimento (unpublished).

[24] E. Hollauer and M. A. C. Nascimento (unpublished).

[25] C. E. Bielschowsky, M. A. C. Nascimento, and E. Hollauer, Quim. Nova (Brazil) 12, 225 (1989).

[26] W. J. Hunt and W. A. Goddard III, Chem. Phys. Lett. 3, 414 (1969).

[27] R. N. S. Sodhi and C. E. Brion, J. Electron. Spectrosc. 34, 363 (1984).

[28] P. S. Bagus and H. F. Schaefer III, J. Chem. Phys. 56, 224 (1972).

[29] C. E. Bielschowsky, G. G. B. de Souza, C. A. Lucas, and H. M. Boechat Roberty, Phys. Rev. A 38, 3405 (1988).

[30] G. G. B. de Souza, C. E. Bielschowsky, C. A. Lucas, and A. C. A. Souza, Phys. Rev. A 42, 1363 (1990).