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Abstract

Correlation effects associated with excitations within the valence shell, and the coupling with single excitations in the virtual space, are examined by CI calculations with virtual orbitals defined by a projection or the IVO scheme. A reasonable description is obtained by a minimal model combining double excitations in the valence with single excitations in the virtual space.

The presence of satellite structures in core photoelectron spectra has been long recognized. At variance with the inner valence region, the general interpretation is however still based on the simple shake theory, although the importance of higher order correlation effects has been stressed in individual systems. In the valence region of molecules the dominant correlation effects are associated with fluctuations of electrons within the valence shell (1,2,3). A CI study of the core region within a minimal basis set has indicated that besides relaxation satellites the most important states are given by double excitations to low-lying empty orbitals, while no fluctuations of the core hole are relevant, except in the case of equivalent atomic sites. This is in marked contrast with the situation found in the valence region, where the strongest effects are associated with such excitations, that is the 2h-1p configurations. Despite the limitations due to the use of a minimal basis set, it is expected that a correct picture is achieved. It is however obvious that an extended basis must be employed for a quantitative description. In order to retain the conceptual and computational simplicity associated with the use of a valence space, it is however necessary to extract a valence complement of the occupied orbitals from the full virtual space. We have here analyzed two possibilities, namely a projection scheme (4), successfully employed in the valence region, and the improved virtual orbital (IVO), or V^{N-1} scheme (5).

Calculations were performed as in previous work (3). The basis employed is (9s,5p/5s,3p) for C, O, N and (5s/3s) for H, plus (2s,2p) Rydberg orbitals in the center of mass (6). Separate SCF calculations were performed for the ground and ionized systems. Intensities were calculated according to the usual expression

$$R_i = \left| \left\langle \Psi_i^{N-1}, a_k \Psi_o^N \right\rangle \right|^2 \qquad\qquad I(\%) = 100 \times R_i/R_o$$

where k is the core orbital considered.

Within the valence space, single, single+double (hereafter referred as 2h-1v and 3h-2v respectively) and full CI were employed both for the neutral and ionized system. In the latter a hole was localized in the relevant core orbital, or delocalized over equivalent orbitals in the case of N_2. Additionally single excitations were allowed in the rest of the virtual space by combining 3h-2v in the valence plus the complete 2h-1p space (referred as 3h-2v+2h-1p), or by employing a maximum excitation level of 2 in the valence space and 1 in the remaining virtuals (3h-2v-1p).

The results for H_2O are reported in figure 1. The 2h-1v results show few lines, with most of the intensity concentrated at ~ 28 eV. This intensity is reduced by a factor of 3 from the value computed in a minimal basis, showing the large effect of relaxation in this case. While the inclusion of higher excitations within the valence shell does not lead to significant variations, the extension to the whole virtual space (2h-1p) gives rise to a splitting of this single line into a multiplet of closely spaced states, possibly because of Rydberg-valence mixing. Small changes are further given by the more extended schemes and also by the use of the IVO orbitals. The results so obtained are in good agreement with the experimental data and those of previous extensive calculations (7,8, 9).

In N_2 a larger difference is afforded by the use of IVO orbitals, especially apparent in the CI within the valence shell. In this case single excitations are unable to give a correct description of the spectrum. The 3h-2v results reported in figure 2 give a reasonable description of the first two peaks, while the structure at the higher energy side in the experimental spectrum (10) is concentrated in few lines, and also the spacings are underestimeted. This structure spreads into several low intensity lines in the 3h-2v+2h-1p and 3h-2v-1p schemes. At the same excitation level the use of projected orbitals gives fewer lines carrying similar intensity over the same energy region. The agreement with the experimental spectrum is reasonable, although a detailed correspondence between the individual peaks is lacking in the higher energy part, and the overall intensity appears to be underestimated. A similar description is however given by previous investigations (11).

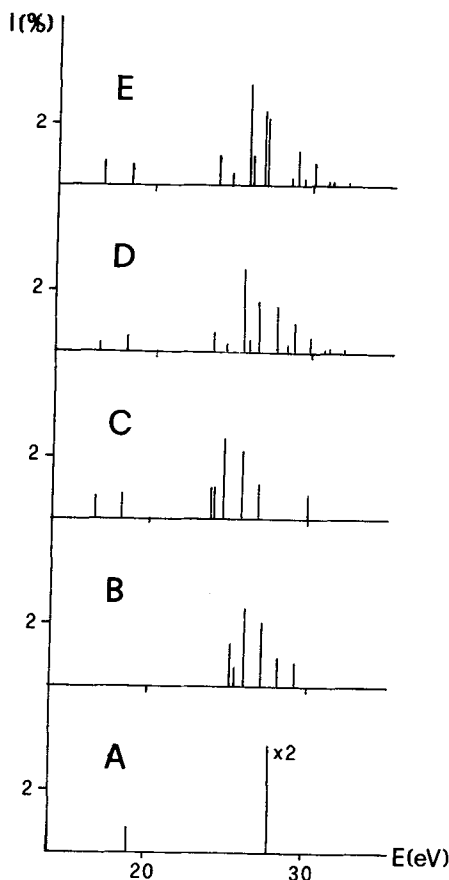Only the projection scheme has been employed for the $2a_1$ (C 1s) spectrum of CO. The relevant re-

Fig. 1. O 1s satellite structure in H_2O.
A: 2h-1v, B: 2h-1p, C: 3h-2v+2h-1p, E: 3h-2v-1p, all with projected orbitals. D: 3h-2v+2h-1p with IVO orbitals. All energies are relative to the main O 1s peak.
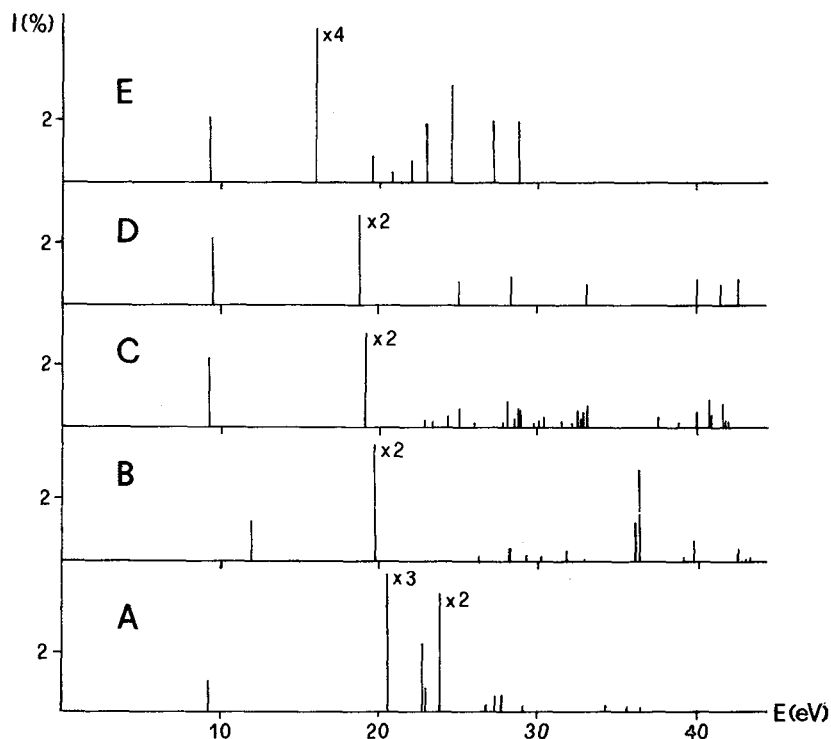
Fig. 2. N 1s satellite structure in N_2. A: 3h-2v, B: 3h-2v+2h-1p, C: 3h-2v-1p, all with IVO orbitals. D: 3h-2v-1p with projected orbitals. E: experimental spectrum (ref. 10). All energies are relative to the main N 1s peak.

levant results are reported in figure 3. Again the coupling to the single excitations in the virtual space gives rise to several lines in the higher energy side. A greater change is apparent in this case in going from the 3h-2v+2h-1p to the 3h-2v-1p scheme. The agreement with the experimental data (10) is less satisfactory. There is still one to one correspondence for the first two peaks (and the results of previous calculations (12)) but the energies are overestimeted and the intensity is calculated much lower. This deficiency is much improved in the valence full CI calculations, indicating the importance of higher excitations in this case. An overall qualitative agreement, like in N_2, is instead obtained for the higher energy part.

   From the results reported it appears that the major deficiency associated with the use of a minimal basis set, namely the concentration of the intensity in few lines and the absence of structure, which is most apparent in the water molecule, is recovered by the schemes employed. Correlations associated with higher excitations are reasonably taken into account by double excitations in the valence shell, even in the simpler 3h-2v+2h-1p scheme. This is particularly convenient for the small dimension of the relevant CI matrices, which allows an easy extension to larger systems.
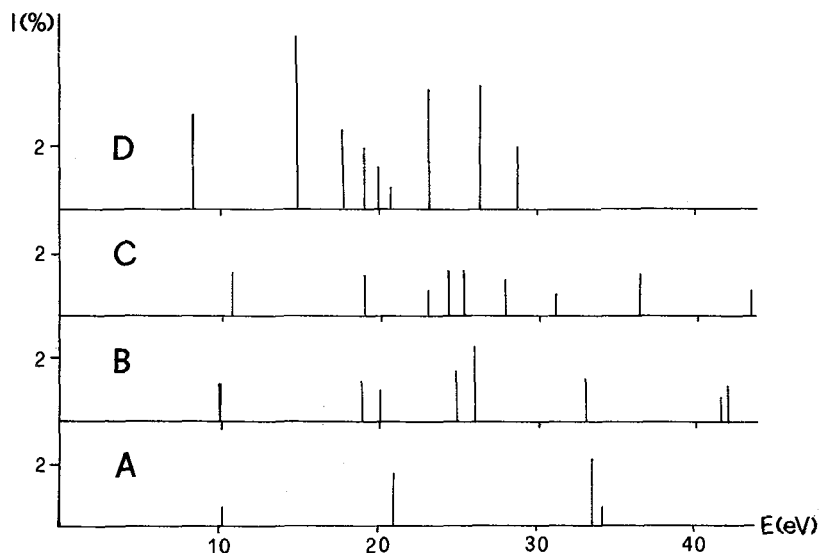
Fig. 3. C is satellite structure in CO. A: 3h-2v, B: 3h-2v+2h-1p, C: 3h-2v-1p, all with projected orbitals. D: experimental spectrum (ref. 10). All energies are relative to the main C 1s peak.

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