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Ab initio Hartree–Fock Calculations of Molecular X-ray Intensities. Validity of One-center Approximations

Hans Ågren

Institute of Quantum Chemistry, University of Uppsala, Box 518, S-751 20 Uppsala, Sweden

Joseph Nordgren

Institute of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden

Ab initio Hartree–Fock calculations of relative X-ray transition probabilities for core hole states of N_2, CO, H_2O and NH_3 have been carried out and compared with the respective high-resolution soft X-ray spectra. The same one-determinental wavefunctions were employed for both initial and final states and the dependence of the X-ray transition moments on the choice of orbitals and of basis set parameters was investigated. In particular, orbitals optimized for a transition state were tested. The use of the one-center intensity model as a guide for the assignment of second row X-ray spectra was justified at both *ab initio* and semiempirical (CNDO) levels of approximation. The breakdown of the MO-picture for inner-valence electrons is demonstrated in the X-ray spectrum of N_2 and the analogy with the corresponding photoelectron bands is pointed out.

Key words: Soft X-ray emission – Molecular X-ray emission – X-ray intensities – One-center approximation.

1. Introduction

The use of computational methods for investigation of molecular electronic spectra has mostly been devoted to the calculation of binding and transition energies. Comparatively less attention has been paid to molecular transition probabilities. Employing LCAO expansion methods, one has approximated band

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intensities in molecular valence photo-electron- [1], Auger- [2] and X-ray spectra [3] by means of one-center calculations of the corresponding transition moments or by weighting empirical atomic intensities with the appropriate expansion coefficients.

A one-center approximation has a particularly simple implementation for molecular X-ray intensities due to the straightforward atomic selection rules that govern dipole transitions. On the basis of this approximation, non-empirical as well as semi-empirical calculations have been carried out for X-ray spectra of several molecules containing second and third row elements [3–7]. Further, for some of the latter compounds the one-center treatment was refined with full two-center calculations [5–7]. However, except for the investigation of the sulphur L-emission spectrum of SF_6 [7], calculations of molecular soft X-ray emission spectra have not yet been properly confronted with highly resolved experimental spectra.

The possible validity of an intensity model based on the one-center approximation has an important consequence in the usefulness of X-ray emission in the study of molecular orbital composition in large organic molecules. Therefore, in order to test the validity of this model and of intensities computed from Hartree–Fock wavefunctions in general, we present in this work one- and full two-center calculations of K X-ray emission intensities for some small molecules and compare the results with well resolved experimental spectra. Both CNDO and *ab initio* calculations have been carried out and for the latter cases the dependence of the intensities on basis set parameters and on the choice of orbitals is investigated.

2. Method and Calculation

In the dipole approximation the relative probability for spontaneous emission is determined by

$$I_{i-j} \sim E^3 |\langle \psi_i | \Sigma\, e\underline{r}_k | \psi_j \rangle|^2 \tag{1}$$

where E is the transition energy and ψ_i and ψ_j are the total wavefunctions for the initial and the final state respectively. In the present work we apply a common set of orbitals for the initial and final states and Eq. (1) is accordingly reduced to

$$I_{i-j} \sim E^3 |\langle \varphi_i | e\underline{r}_1 | \varphi_j \rangle|^2 \tag{2}$$

where, in the case of soft X-ray emission, φ_i is a core electron orbital and φ_j denotes a valence electron orbital. In going from Eq. (1) to Eq. (2) we have implicitly also assumed Born–Oppenheimer separability of electronic and nuclear motion and the so-called crude adiabatic approximation, i.e. the electronic transition moment is assumed to be constant for different nuclear coordinates. The energy dependence of the spectral function will then be determined by expression (2) modulated by a sum of squared overlap integrals of vibrational wavefunctions, the Franck–Condon factors, which will govern the shape of the various X-ray emission bands. The possibility to deduce information about the core hole energy curves from Franck–Condon analysis of experimental X-ray band shapes has been demonstrated recently for the presently investigated molecules [8, 9].

In the one-center model Eq. (2) is further simplified. This model was originally introduced by Manne [3] and applied to K-spectra of some second-row elements. In order to make the present work more self-contained we give a brief outline of the one-center model below. Basically it comprises two assumptions. Firstly, the vacancy of the initial state is assumed to be strongly localized to one atomic site. This is a natural assumption in the case of X-rays since core vacancies then are involved. Secondly, the subsequent X-ray deexcitation is assumed to reflect the local behaviour of the wavefunction around that atomic site, that is, in the LCAO picture the local atomic contributions to the different molecular orbitals determine the X-ray spectrum. From these assumptions and from ordinary atomic dipole selection rules we obtain the following expression for the relative intensity of the jth molecular orbital transition after having ionized a core electron of angular symmetry l.

$$I^j_{\text{X-ray}} \sim E^3 \sum_{k=l+1\pm 2i} W_{lk}\langle X_l|\underline{r}_1|X_k\rangle^2 (C^j_k)^2 \tag{3}$$

i is an integer, k denotes the symmetry of (valence) atomic orbitals, $\langle X_l|\underline{r}_1|X_k\rangle$ the radial matrix elements and C^j_k is the expansion coefficient of the atomic orbital X_k in the jth MO. W_{lk} is a factor originating in the integration of the angular parts of the atomic orbitals.

In a previous application of Eqs (2) and (3) to the $L_{\text{II,III}}$ X-ray spectrum of the SF_6 molecule [7] it was found that neither of the two basic assumptions were fullfilled; the small off-center parts of the "S2p"-orbital gave non-negligible contributions to the total transition moment and the two-center "cross-transitions" were also found to be significant. On the basis of these findings it was argued that the applicability of the one-center model is rather limited for L-emission of third row elements.

For K-emission of second row elements, however, which is the subject of the present investigation, the initial 1s hole is strongly localized and expression (3) will then also assume its simplest form:

$$I^j_{\text{X-ray}} \sim E^3 (C^j_{2p})^2. \tag{4}$$

For calculations employing basis sets larger than a minimal one, we replace Eq. (4) by:

$$I^j_{\text{X-ray}} \sim E^3 \sum_{k\in 2p} (C^j_k)^2 \tag{5}$$

in which either the net-atomic or the gross-atomic form of the MO-population routine may be used. In the present work we will evaluate the quality of expression (5) in relation to that of expression (2) and compare the results with experimental X-ray intensities.

A programme was therefore written for the calculation of transition moment integrals (Eq. (2)) over molecular orbitals expanded in contracted and symmetry adapted cartesian gaussian basis functions. It was further implemented with the MOLECULE–ALCHEMY programme package [10] for open-shell Roothaan restricted Hartree–Fock calculations. The programme made use of the compact formulation of gaussian expansions of molecular properties as outlined by Matsuoka [11].

Two basis sets [12], $2Z$ and $3Z$, were employed in the present work. The contraction schemes for these basis sets were $(9s5p)-\langle 4s, 2p\rangle$ and $(11s, 7p)-\langle 6s, 4p\rangle$ for C, N and O and $(5s)-\langle 2s\rangle$ and $(6s)-\langle 3s\rangle$ for H. All calculations were carried out at the experimental ground state geometries.

3. Results and Discussions

Compounds with core hole states localized to different atomic species exhibit X-ray spectra connecting the valence states with the respective core states in well separated energy intervals. Symmetry considerations then put different constraints on the allowed dipole transitions from the common set of valence orbitals. The CO X-ray spectrum [13] is illustrative in this context since all dipole transitions are symmetry allowed in the oxygen as well as in the carbon part of the spectrum. The two parts show quite different characteristics both with respect to the band shapes and the band intensities. The delocalized 1π orbital is intensively represented in both CO spectra, whereas the 4σ band is absent in the carbon spectrum while it shows appreciable intensity in the oxygen spectrum. The 5σ band is comparatively more intense in the carbon than in the oxygen spectrum. Finally, the 3σ band is missing in both spectra. It is immediately noted that the main features of the spectrum are reproduced by a coarse consideration of the one-center $2p$ character of the different orbitals. As can be seen in the columns 2, 3 and 4 in Tables 1–5, which show CNDO (gross and *ab initio* (net and gross) $2p$ population numbers respectively, the CO spectrum as well as the X-ray spectra of the N_2, H_2O and NH_3 molecules are fairly well reproduced already at the level of the one-center approximation. It should be noted that some arbitrariness is involved in the choice of net or gross atomic population number as a guide for the intensities.

The results of the calculations of the full transition moments are presented in columns 5–8 in Tables 1–5. It is observed that the magnitudes of the two-center contributions generally are rather small, though some significance may be attributed to such contributions for inner valence bands. As an example, the CO Cls–O2s transition moment is rather prominent. However, considering the dependence of the transition moments on the choice of reference state for orbital optimization and of the degree of agreement between the calculated and the experimental results, one finds that not much is gained turning from one-center to full two-center calculations without paying further attention to the description of the wave functions involved.

An idea of the basis set dependence of the calculated full X-ray transition moments is gained by considering columns 5 and 6 in Tables 1–5, which show the results of the ground state calculations for double zeta and triple zeta basis sets.

Key to Tables

Tables 1–5. Calculated relative K X-ray emission intensities for N_2, oxygen CO, carbon CO, H_2O and NH_3.

Column
2. Intensities from CNDO gross atomic $2p$-populations.
3. Intensities from *ab initio* ground state ($3Z$) net atomic $2p$-population.
4. Intensities from *ab initio* ground state ($3Z$) gross atomic $2p$-populations.
5. Full X-ray transition moments from ground state ($2Z$) wavefunctions.
6. Full X-ray transition moments from ground state ($3Z$) wavefunction.
7. Full X-ray transition moments from core hole state wavefunction.
8. Full X-ray transition moments from transition state wavefunction.
9. Experimental densitometer intensities.

Table 1. N_2 X-ray transition intensities

1	2	3	4	5	6	7	8	9
Final state	CNDO gross	*ab initio* net	*ab initio* gross	$GS(2Z)^a$	$GS(3Z)^a$	$1\sigma^{-1\,b}$	TRANS[b] $1\sigma^{-1}-3\sigma_g^{-1\,b}$	Experiment [13]
$3\sigma_g^{-1}$	0.31	0.45	0.54	0.53	0.56	0.37	0.66	0.58
$1\pi_u^{-1}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$2\sigma_u^{-1}$	0.14	0.07	0.11	0.11	0.12	0.16	0.16	0.16
$2\sigma_g^{-1}$	0.10	0.07	0.10	0.17	0.18	0.13	0.10	—

[a] Sum over X-ray transition probabilities for $1\sigma_g^{-1}$ and $1\sigma_u^{-1}$ states. Ionization probability and Auger yield for these two states is assumed equal.

[b] Broken symmetry solutions employed.

Table 2. CO oxygen X-ray transition intensities

1	2	3	4	5	6	7	8	9
Final state	CNDO gross	*ab initio* net	*ab initio* gross	$GS(2Z)$	$GS(3Z)$	$1\sigma^{-1}$	TRANS $1\sigma^{-1}-4\sigma^{-1}$	Experiment [13]
$5\sigma^{-1}$	0.14	0.12	0.22	0.11	0.12	0.08	0.00	0.28
$1\pi^{-1}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$4\sigma^{-1}$	0.38	0.29	0.26	0.37	0.39	0.37	0.51	0.38
$3\sigma^{-1}$	0	0.04	0.09	0.07	0.07	0.06	0.08	—
$2\sigma^{-1}$	0	0	0	0	0	0	0	—

Table 3. CO carbon X-ray transition intensities

1	2	3	4	5	6	7	8	9
Final vacancy	CNDO gross	*ab initio* net	*ab initio* gross	$GS(2Z)$	$GS(3Z)$	$1\sigma^{-1}$	TRANS $2\sigma^{-1}-1\pi^{-1}$	Experiment [13]
$5\sigma^{-1}$	0.73	0.95	0.74	1.09	1.09	0.91	0.84	0.59
$1\pi^{-1}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$4\sigma^{-1}$	0.02	0.06	0.04	0.08	0.09	0.04	0.03	—
$3\sigma^{-1}$	0	0.10	0.16	0.32	0.36	0.25	0.24	—

Table 4. H_2O X-ray transition intensities

1	2	3	4	5	6	7	8	9
Final state	CNDO gross	*ab initio* net	*ab initio* gross	$GS(2Z)$	$GS(3Z)$	$1a_1^{-1}$	TRANS $1a_1^{-1}-1b_1^{-1}$	Experiment [19]
$1b_1^{-1}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.83
$3a_1^{-1}$	0.71	0.65	0.76	0.77	0.77	0.89	0.77	1.0
$1b_2^{-1}$	0.57	0.41	0.57	0.55	0.54	0.65	0.56	0.94
$2a_1^{-1}$	0	0.02	0.03	0.04	0.04	0.05	0.04	—

Table 5. NH_3 X-ray transition intensities

1	2	3	4	5	6	7	8	9
Final state	CNDO gross	*ab initio* net	*ab initio* gross	$GS(2Z)$	$GS(3Z)$	$1a_1^{-1}$	TRANS $1a_1^{-1}-4a_1^{-1}$	Experiment [20]
$3a_1^{-1}$	0.68	0.85	0.53	0.80	0.79	0.77	0.79	1.0
$1e^{-1}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.89
$2a_1^{-1}$	0	0.18	0.09	0.03	0.03	0.03	0.05	—

The numbers in the two columns are consistent, suggesting that the commonly used $2Z$ basis sets are flexible enough for the purpose of computing molecular X-ray intensities.

In columns 7 and 8 finally, we show X-ray transition moments computed from orbitals optimized for different states. A great saving in the computational procedure is gained by using a common set of orbitals for the initial and final states. However, since the X-ray transition connects the valence hole states with a highly excited core hole state, a rather significant contribution of relaxation to the intensities must be anticipated in line with the strong influence of relaxation on X-ray transition energies and band shapes [8–9]. The tables display results for orbitals optimized for the ground state, the initial $1s$ core hole state and for a transition state assuming 1.5 occupancy in the $1s$ shall and 1.5 occupancy in a (non-degenerate) valence shell. The latter set of orbitals represent an intermediate choice with respect to relaxation between the initial and the particular final state, but does not account for differences in relaxation between the various final valence hole states. To account for this latter effect one has to employ explicit non-orthogonal determinant calculations. The multiconfigurational transition operator procedure outlined by Godefroid et al. may be an appropriate alternative [21].

The present results indicate a fluctuation of typically 20% of the X-ray intensities when different sets of orbitals are employed. Also, one can note from calculations of various other one-electron properties using SCF wavefunctions that a deviation of 10–20% from experiment very well may be encountered even at the HF limit [15]. However, in a few cases the divergence between the present experimental and calculated results exceeds the experimental accuracy set by the photographic recording technique and by the possible presence of unresolved satellite background. For example, experimental evidence of transitions from inner-valence orbitals are mostly lacking, whereas the HF-calculations predict small but significant intensities mainly of two-center origin. This discrepancy may be explained by appreciable correlation effects in the final ionic states. Large correlation effects for inner valence hole states have been analyzed by Shirmer and co-workers [16, 17] in connection with the interpretation of the photoelectron spectra of the presently investigated molecules. They found a complete breakdown of the molecular orbital picture, with e.g. the N_2 $2\sigma_g$ band split into a large number of components of approximately equal intensity. A corresponding situation is encountered in the X-ray spectrum. As can be seen in Fig. 1, which shows the full first order X-ray spectrum of N_2, the $2\sigma_g$ band is considerably broader than the other valence bands. However, the X-ray spectrum is expected to be more complex, primarily due to the fact that there are many possible initial correlation states for the X-ray transitions. This kind of final ionic "semiinternal"

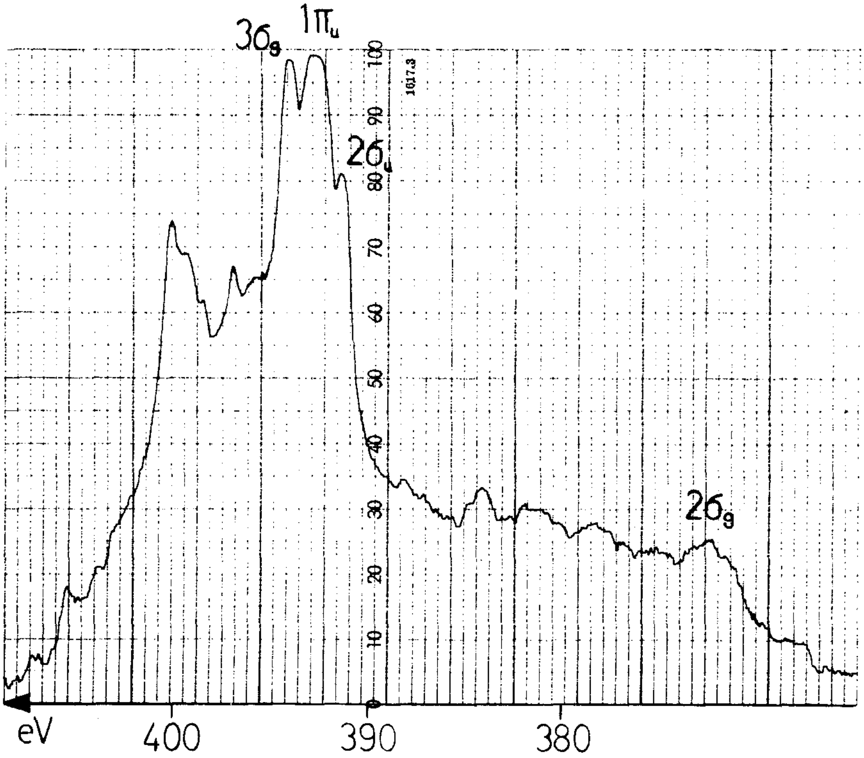

Fig. 1. The first order K X-ray emission spectrum of N_2

CI resonances in X-ray spectra was also observed in the high resolution L-emission spectrum of argon [18] in which a number of transitions to $3s^{-1}$ correlation states were assigned.

One may also anticipate strong correlation contributions to transition rates for outer valence orbitals, e.g. for transitions from the 1π orbitals of N_2 and CO. For N_2, this correlation is strong enough to invert the order of the calculated one-particle 1π and $3\sigma_g$ transition energies [8]. From the discussion above it seems appropriate to advocate CI-procedures for a refinement of the present calculations of X-ray intensities.

4. Conclusions

The main conclusion of this work is that when assigning X-ray emission spectra of second row molecules by means of one-particle HF calculations not much is gained by invoking two-center transition moments in the intensity analysis since these contributions are found to be relatively small in magnitude. It seems that the use of the CNDO approximation is justified when aiming at explaining the coarse features of second row K-spectra, a result which might be important for the analysis of larger molecules, where *ab initio* calculations are not very feasible. When *ab initio* calculations are feasible, the present investigations recommend the use of net or gross atomic population numbers from ground state orbitals and the use of ordinary double zeta basis sets.

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