PHYSICAL REVIEW A, VOLUME 63, 042514

Single-atom approximation for $K\beta$-to-$K\alpha$ x-ray intensity ratios in chemical compounds of $3d$ elements

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(Received 2 February 2000; published 22 March 2001)

The single-atom approximation for the $K\beta$-to-$K\alpha$ x-ray intensity ratios for chemical compounds of $3d$ elements has been tested with the discrete-variational $X\alpha$ (DV-$X\alpha$) molecular-orbital (MO) method. The effective numbers of electrons in each atomic shell are obtained with the DV-$X\alpha$ method and used to calculate the $I(K\beta)/I(K\alpha)$ ratio in the single-atom approximation. The calculated results are in good agreement with the DV-$X\alpha$ MO values for octahedral symmetry, but systematically smaller for tetrahedral symmetry. The reason for this discrepancy is ascribed to be the $K\beta_{2,5}$ component, which is appreciable in some compounds with the tetrahedral symmetry.

DOI: 10.1103/PhysRevA.63.042514 PACS number(s): 33.20.Rm, 36.20.Kd, 78.70.En, 82.80.Ej

The $K\beta$-to-$K\alpha$ x-ray intensity ratios, $I(K\beta)/I(K\alpha)$, in the chemical compounds of $3d$ elements have received special attention both experimentally and theoretically, because they depend on the chemical environments [1–15] as well as the excitation modes [16–22]. Recently, we have shown [7] with the discrete-variational (DV) $X\alpha$ molecular-orbital (MO) method that the chemical effect on the $I(K\beta)/I(K\alpha)$ ratios depends on the symmetry property of molecules. We have also pointed out [22] that the change in the $I(K\beta)/I(K\alpha)$ ratios in different excitation modes is ascribed to the difference in the effective number of $3d$ electrons, N_{3d}, before the x-ray emission. Furthermore, we found [23] that when the $I(K\beta)/I(K\alpha)$ ratios for chemical compounds are plotted as a function of N_{3d}, they are on a straight line with a negative slope and the value of the slope depends on the molecular symmetry.

The above results indicate that the screening effect of $3d$ electrons in the molecule plays an important role in the emission of $K\beta$ x rays. Considering this fact, we can assume that if we know the effective number of electrons in each shell of the atom of interest from the MO calculation, the $I(K\beta)/I(K\alpha)$ ratio in the molecule can be obtained by a single-atom calculation for the x-ray transition probabilities with valence electron configuration corresponding to these effective numbers of electrons. This *single-atom* approximation has been often used for the calculations of x-ray emission rates in molecules. For example, Band *et al.* [4] used this method to calculate the chemical effect on the $I(K\beta)/I(K\alpha)$ ratios in Cr and Mn compounds.

Recently, Polasik [24] calculated the $K\beta$-to-$K\alpha$ x-ray intensity ratios for atoms of all $3d$ transition metals with the multiconfiguration Dirac-Fock method [25] including the Breit interaction and quantum electrodynamic corrections. For $3d$ elements, the atoms with $3d^{m-2}4s^2$, $3d^{m-1}4s^1$, and $3d^m$ configurations were considered and the dependence of $I(K\beta)/I(K\alpha)$ ratios on the valence electron configuration was studied. Polasik's results were used to analyze the experimental results [15,26] to determine the effective number of valence electrons in the chemical compounds.

Since the atomic calculations are much easier than the molecular ones, it is very useful to study the x-ray emission rates for chemical compounds with the single-atom approximation, if this model can be successfully used. The purpose of the present work is to test the validity of the single-atom approximation for the $I(K\beta)/I(K\alpha)$ ratios in $3d$ elements.

It should be noted, however, that the single-atom approximation is different from the *single-center* approximation, which we have studied already [27]. In the case of the single-center approximation, the transition matrix elements for the x-ray emission are calculated between the initial- and final-state MO wave functions, but the contributions from other atoms, i.e., the interatomic transitions, are neglected. On the other hand, in the single-atom approximation the transition probabilities between two atomic orbitals (AO's) are calculated for the atom with an appropriate electron configuration.

In the present work, we have performed the MO calculations for several chemical compounds of Cr and Mn with the DV-$X\alpha$ method [28]. For simplicity, we chose the molecules with the tetrahedral (T_d) and octahedral (O_h) symmetry. The effective number of electrons in each shell of Cr and Mn is obtained with the DV-$X\alpha$ MO method from Mulliken's population analysis [29] and is listed for some chemical compounds of Cr and Mn in Tables I and II together with the electron configuration for the isolated atom. The data used for the MO calculations for these compounds, such as cluster, symmetry, and bond length, are found in our previous paper [7]. We used the frozen-orbital approximation to calculate x-ray emission rates and all the calculations were made with the ground-state wave functions, in a similar manner to the numerical tables of Manson and Kennedy [30] and Scofield [31].

TABLE I. Mulliken's population analysis of Cr compounds.

Shell	Cr	CrO$_4{}^{2-}$	Cr$_2$O$_7^{2-}$	CrO$_2$	CrCl$_3$	CrCl$_2$
1*s*	2	2	2	2	2	2
2*s*	2	2	2	2	2	2
2*p*	6	6	6	6	6	6
3*s*	2	2	2	2	2	2
3*p*	6	6	6	6	6	6
3*d*	5	3.44	3.48	3.56	4.21	4.42
4*s*	1	0.06	0.12	0.25	0.43	0.36
4*p*		0.28	0.34	0.08	0.23	0.18

Using the effective numbers of electrons in the tables, the atomic Hartree-Fock-Slater ($X\alpha$) calculations have been carried out and the x-ray transition probabilities have been evaluated in the dipole approximation [30,32]. Throughout all the calculations, Slater's statistical exchange coefficient was kept at $\alpha = 0.7$ in order to compare with the MO calculations. The results are shown in Table III and compared with the values calculated with the MO wave functions. The MO x-ray emission rates were estimated in a manner similar to our previous works [7,22], using the MO wave functions obtained in the DV-$X\alpha$ calculations described above. The transition matrix elements between two MO's in the dipole approximation were evaluated in the DV integration scheme [33].

The calculated values for atoms are in agreement with the tabulated values: 0.1150 [30] and 0.1153 [31] for Cr and 0.1192 [30] and 0.1195 [31] for Mn. The reason for the slightly smaller values in Table III is ascribed to the statistical exchange coefficient used by us, $\alpha = 0.7$. When we adopt $\alpha = 1$, the corresponding values coincide with the values of Manson and Kennedy [30]. This fact indicates the validity of the DV integration method for calculations of dipole matrix elements. The values of Scofield were obtained with the relativistic wave functions including all multipoles and are slightly larger than the nonrelativistic ones.

It is clear from Table III that for the O_h symmetry the single-atom approximation can well reproduce the $K\beta$-to-$K\alpha$ ratios in the MO calculations. However, in the case of T_d symmetry the AO calculation gives a smaller value than the MO calculation. We have already shown [7] that the results of MO calculations are qualitatively in agreement with the experimental values. According to our results with the single-center approximation [27], the contributions from the interatomic transitions are negligible for the $I(K\beta)/I(K\alpha)$ ratios in the 3*d* elements. We have already pointed out [7] that for compounds with T_d symmetry, the presence of the $K\beta''$ and $K\beta_{2,5}$ lines increases the $I(K\beta)/I(K\alpha)$ ratios, while in the O_h symmetry their contributions are small. Considering these facts, the present results suggest that the contribution from one or both of these satellite lines is not properly taken into account in the single-atom approximation.

TABLE II. Mulliken's population analysis of Mn compounds.

Shell	Mn	MnO$_4{}^-$	MnO$_4{}^{2-}$	MnO$_2$	MnCl$_2$
1*s*	2	2	2	2	2
2*s*	2	2	2	2	2
2*p*	6	6	6	6	6
3*s*	2	2	2	2	2
3*p*	6	6	6	6	6
3*d*	5	4.49	4.67	4.68	5.48
4*s*	2	0.11	0.24	0.28	0.38
4*p*		0.44	0.40	0.09	0.18

TABLE III. Comparison of atomic and molecular calculations of $I(K\beta)/I(K\alpha)$ ratios for Cr and Mn compounds.

Compound	Symmetry	Atomic	Atomic$+K\beta_{2,5}$	Molecular
Cr		0.114		
CrO$_4{}^{2-}$	T_d	0.119	0.123	0.123
Cr$_2$O$_7{}^{2-}$	T_d	0.119	0.123	0.122
CrO$_2$	O_h	0.118		0.117
CrCl$_3$	O_h	0.116		0.115
CrCl$_2$	O_h	0.115		0.115
Mn		0.118		
MnO$_4{}^-$	T_d	0.120	0.124	0.124
MnO$_4{}^{2-}$	T_d	0.120	0.122	0.121
MnO$_2$	O_h	0.119		0.119
MnCl$_2$	O_h	0.117		0.116

In order to test this assumption, the energy eigenvalues of atomic and molecular calculations for MnO$_4{}^{2-}$ are shown in Table IV. For MO's, the components of Mn AO's are also given. From a comparison of the energy eigenvalues between AO's and MO's, the energy of the 4*p* orbital in the atomic calculation is close to the energy of the 4t_2 orbital in the MO calculation, but is far from that of the 6t_2 orbital. As can be seen in our previous work [7], the $K\beta''$ line corresponds to the $4t_2 \rightarrow 1s$ transition and the $K\beta_{2,5}$ line comes from the $6t_2 \rightarrow 1s$ transition. The x-ray emission rates depend on the number of electrons, transition energy, and shape of the wave functions. In the single-atom approximation, only the effective numbers of electrons are taken into consideration. If we assume that the AO and MO wave functions have similar form, Table IV suggests that in the single-atom approximation the intensity of the $K\beta''$ line is taken into ac-

TABLE IV. Energy eigenvalues (eV) of atomic and molecular calculations for MnO$_4{}^-$.

AO	Population	Energy	MO	Population	Energy	Mn component
3*d*	4.49	−27.031	5a_1	2	−18.805	4*s*
4*s*	0.11	−19.844	4t_2	6	−17.172	3*p*,3*d*,4*p*
4*p*	0.44	−14.285	5t_2	6	−4.866	3*d*,4*p*
			1e_1	4	−4.835	3*d*
			6a_1	2	−3.135	4*s*
			6t_2	6	−2.659	4*p*
			1t_1	6	1.220	

count, but the contribution from the $K\beta_{2,5}$ line is considerably underestimated. On the other hand, in the single-center approximation, the contributions from both lines are involved, because we used the MO states and their wave functions.

As a simple approximation, we assume that the contribution from the $6t_2$ orbital is not included and we add the contribution from the intensity of the $K\beta_{2,5}$ ($6t_2 \rightarrow 1s$) line from the MO calculations to the $I(K\beta)/I(K\alpha)$ ratios in the single-atom approximation. The obtained results are also listed in Table III for compounds with T_d symmetry. It is clear that the total $I(K\beta)/I(K\alpha)$ ratios for the compounds with the T_d symmetry are in good agreement with the values of the MO calculations. This fact indicates that the single-atom approximation cannot take into account the contribution from the $K\beta_{2,5}$ line.

In our previous paper [7], we pointed out that the $I(K\beta)/I(K\alpha)$ ratios of Band *et al.* in the multiple-scattering (MS) $X\alpha$ method [4] are systematically larger than our DV-$X\alpha$ values. They carried out the MO calculations with the MS-$X\alpha$ method and calculated the $I(K\beta)/I(K\alpha)$ ratios in the single-atom approximation using the results obtained from the MO calculations. Comparison with our results was made in the form of relative $I(K\beta)/I(K\alpha)$ ratios to the standard clusters $CrO_4{}^{2-}$ and $MnO_4{}^{-}$, which have the T_d symmetry, and the calculated values for other compounds were expressed as the ratio relative to the corresponding standard values. If the single-atom approximation underpredicts the $I(K\beta)/I(K\alpha)$ ratios in the T_d symmetry, the relative $I(K\beta)/I(K\alpha)$ ratios become smaller by taking into account the intensity of the $K\beta_{2,5}$ line. The relative ratio of the $I(K\beta)/I(K\alpha)$ ratio to the standard value in the single-atom approximation to that of the MO calculation is estimated from Table III to be 0.967 for $CrO_4{}^{2-}$ and 0.968 for $MnO_4{}^{-}$, respectively. Using these values as a correction factor to the value in the single-atom approximation, we can modify the relative $I(K\beta)/I(K\alpha)$ ratios of Band *et al.* [4] to be 0.932 for $CrCl_3$ and 0.935 for MnS. The values thus obtained are in agreement with our DV-$X\alpha$ values, 0.942 for $CrCl_3$ and 0.935 for MnS [7].

In the present work, we used the frozen-orbital approximation. It is well known that for $3d$ elements the calculated values of the $I(K\beta)/I(K\alpha)$ ratios in this approximation are smaller than the experimental values [34]. Scofield [35] pointed out this discrepancy due to a neglect of the exchange effect and nonzero overlap integrals in the matrix elements. His theoretical values for atoms in the relaxed-orbital approximation with both effects are in good agreement with the measured ones.

In the case of molecules, such calculations have been performed only for simple molecules with light elements, because of the numerical accuracy in multicenter integration. In the case of CO molecules, the relative x-ray intensity ratios in the frozen-orbital and relaxed-orbital approximations are almost the same, although the absolute emission rates are different [36–38]. For heavier elements and for complex geometry, such as T_d and O_h symmetry, the $I(K\beta)/I(K\alpha)$ ratios in two approximation would be different. Unfortunately, numerical errors for overlap integrals increase for a large number of atomic orbitals and for complex geometry. Nevertheless, it is hoped that in the future the $I(K\beta)/I(K\alpha)$ ratios will be performed using MO wave functions with the exchange and overlap effects for chemical compounds of $3d$ elements.

In conclusion, we have calculated the $I(K\beta)/I(K\alpha)$ ratios for some compounds of Cr and Mn with T_d and O_h symmetry in the single-atom approximation. The calculations of the atomic x-ray transition probabilities were performed in the dipole approximation using the effective number of electrons estimated from the DV-$X\alpha$ MO calculations. The obtained results for the $I(K\beta)/I(K\alpha)$ ratios are compared with the values from the DV-$X\alpha$ MO wave functions. For compounds with O_h symmetry, the values obtained in the single-atom approximation are in good agreement with those of the MO calculations, while in the T_d symmetry the former values are systematically smaller than the latter. This discrepancy is ascribed to the fact that the single-atom approximation cannot take into account the contribution from the $K\beta_{2,5}$ line, the contribution of which is negligible in the O_h symmetry but appreciable in the T_d symmetry. The sum of the intensity of the $K\beta_{2,5}$ line and the $I(K\beta)/I(K\alpha)$ ratio in the single-atom approximation agrees well with results of the MO calculations.

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