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CHROMIUM HEXACARBONYL**

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FULL-POTENTIAL SCATTERED-WAVE X.A.N.E.S. CALCULATIONS
 FOR CHROMIUM HEXACARBONYL

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Abstract

Using the recently implemented and tested non-muffin-tin scattered-wave method of Natoli *et al.* we calculated the Cr K-edge XANES of the model system chromium hexacarbonyl, to determine the size and nature of non-muffin-tin corrections, and to get some idea of the seriousness of the remaining approximations in current *ab initio* calculations. After summarizing our progress with the non-muffin-tin method we present the results of our calculations for chromium hexacarbonyl, discussing their significance and the implications for XANES calculations in general. In particular, we report a previously hidden sensitivity of the results to details of the construction of the one-electron potential.

In previous work^{1,2,3} we have implemented and tested the full-potential scattered-wave (FP-SW) theory of Natoli *et al.*⁴ for the calculation of bound and continuum electronic states in molecular clusters, with particular application to core-level photoionization and X-ray absorption near-edge structure (XANES). This is an extension of the "muffin-tin" (MT) SW theory of Johnson and co-workers⁵ (for bound states) and Dill and Dehmer⁶ (for continuum states, implemented for XANES in Refs. 7 and 8). The new SW theory avoids the usual MT approximation to the electron-molecule potential, allowing the full potential to be used directly. In this way it is possible to improve on the usual results of *ab initio* XANES calculations, which are often quite poor — particularly in open, covalently bonded systems for which the MT approximation is bad.

The essence of the FP-SW method is the partition of molecular space and the solution of Schrödinger's equation in each region separately. The atoms are enclosed in mutually disjoint spheres centred on their nuclei and the whole collection enclosed in an outer sphere (OS). In an atomic sphere region (ASR) the potential is represented as a spherical harmonic expansion (SHX), the

TABLE I. Comparison of the (negative of the) bound-state energy eigenvalues (in Rydbergs) for H_2^+ from the program ENESHX (for the three program modes) and the exact values from Ref. 9. The proton separation was 2 au and the partition had an OS of radius 2 au containing the two hydrogen spheres each of radius 1 au. We calculated the ten lowest eigenvalues in the irreducible representations A_{1g} , A_{2u} , E_{1g} and E_{1u} of the point group $D_{\infty h}$.

	$1a_{1g}$	$2a_{1g}$	$3a_{1g}$	$4a_{1g}$	$1a_{2u}$	$2a_{2u}$	$3a_{2u}$	$4a_{2u}$	$1e_{1g}$	$1e_{1u}$
L=0	2.0720	0.7041	0.4560	0.3487	1.2880	0.4975	0.2697	0.2499	0.4465	0.8887
+L>0	2.1091	0.7077	0.4733	0.3512	1.3115	0.5070	0.2731	0.2533	0.4540	0.8651
+IR	2.1897	0.7209	0.4710	0.3553	1.3343	0.5109	0.2747	0.2533	0.4533	0.8559
EXACT	2.2053	0.7217	0.4716	0.3554	1.3351	0.5108	0.2746	0.2533	0.4534	0.8576

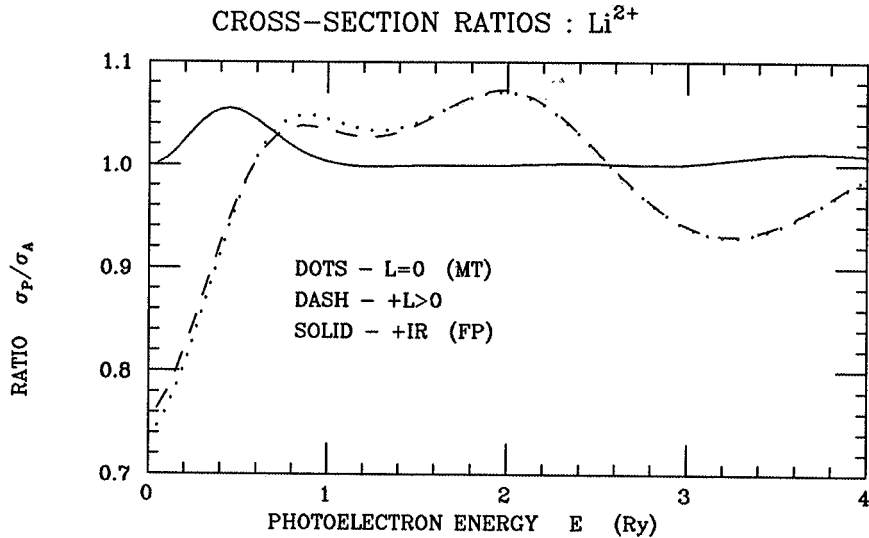


Fig. 1. Comparison (as ratios) of the photoionization cross-sections of Li^{2+} from the program CNTSHX (for three program modes) with exact analytic values from Ref. 10. The partition had a lithium sphere of radius 4 au coordinated octahedrally by six empty spheres of radius 1.5 au all enclosed in an OS of radius 7 au; ensuring that the MT approximation was a sufficient distortion of the true potential that the FP program results gave a significant improvement.

higher multipoles of which cause the radial Schrödinger equations to be coupled giving non-diagonal t -matrices when integrated out from the appropriate boundary conditions at $r = 0$. The same is true for the radial equations in the extra-molecular region (EMR — that outside the OS), which are integrated in from the boundary conditions at infinity. The varying potential in the remaining interstitial region (IR) influences the inter-atom propagation of the photoelectron through its own t -matrix which, in our present implementation, is calculated in the Born approximation. Within this framework the MT approximation consists in retaining only the monopole part of the potential in the ASRs and EMR, and making the IR potential constant (usually equal to its average over the IR).

The program suite that we have developed has two main FP-SW programs — ENESHX which calculates bound-state eigenvalues and CNTSHX which calculates photoionization cross-sections. We tested ENESHX with the hydrogen molecular ion H_2^+ and CNTSHX with a doubly ionized lithium “pseudo-cluster” Li^{2+} so that the results could be compared with the analytic values.^{9,10} The most important of these may be seen in Tab. I and Fig. 1. The programs were run in three modes, corresponding to the successive introduction of the non-MT parts of the potential. The first, denoted “ $L = 0$ ”, corresponds to the MT version of the potential. The second, denoted “ $+L > 0$ ”, introduces the higher multipole parts of the potential in the ASRs and the EMR; while the third, denoted “ $+IR$ ”, then introduces the true non-constant potential in the IR to give the full potential. Based on these results, and others discussed fully in Refs. 2 and 3, we are confident that our theory and its implementation are valid.

Although the programs are at the beginning of their developmental life they are flexible enough to accommodate a wide variety of molecular types — depending on the computing resources available. Thus, to show what practical calculations are possible with the level of computing power generally available, we chose the chromium hexacarbonyl $\text{Cr}(\text{CO})_6$ system for our first investigations. This system consists of a central chromium atom coordinated by six carbonyl ligands in an octahedral configuration with the carbons adjacent to the chromium. It exemplifies all of the worst physical features from the point of view of *ab initio* XANES calculations; being very open, with multiple covalent bonds, and containing several different atomic species. Indeed the MT approximation is bad, with potential discontinuities of several Rydbergs at atomic sphere boundaries^{1,2} — comparable

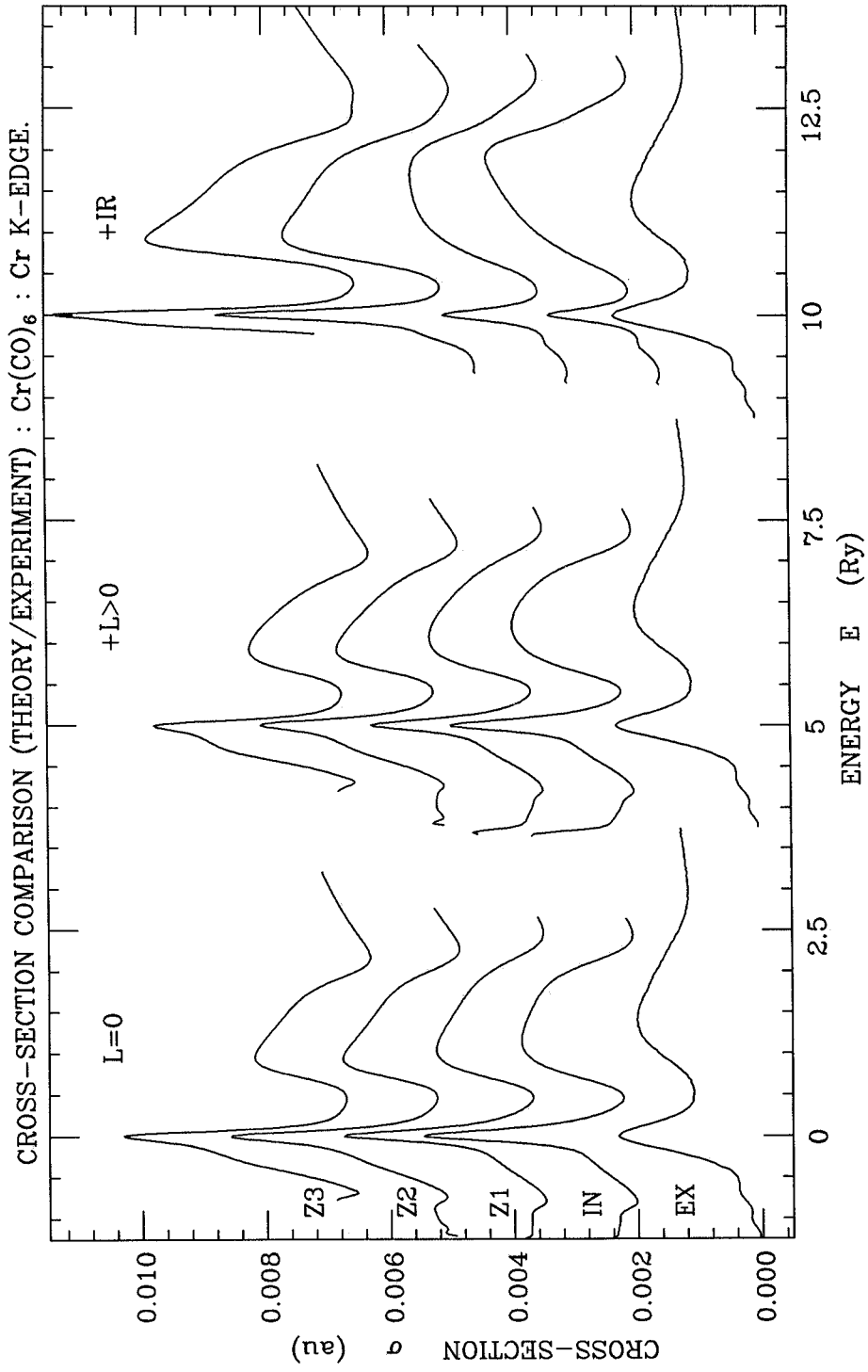


Fig. 2: Theoretical (IN,Z1,Z2,Z3) and experimental (EX) spectra for model system in 3 program modes.

with the range of photoelectron energies in the XANES region.

For the $\text{Cr}(\text{CO})_6$ calculations with CNTSHX we constructed a representation of the full potential, according to the method in Refs. 1 and 2 (Chap. 4), from the free-atom orbitals of Clementi and Roetti.¹¹ For the exchange-correlation potential we used Slater's $X\alpha$ approximation with an average value for the parameter α of 0.74893. We calculated only the continuum cross-sections from the Cr 1s level to the dipole-allowed T_{1u} final states. (Thus no pre-edge, bound-state transitions are included.) No attempt was made to model possible inelastic loss mechanisms. Since we could not use self-consistent electron densities we tried four different final-state potentials. The first, "IN", was just the same as the ground state potential that we constructed above. The others, "Z1", "Z2" and "Z3", were three versions of the so-called Z+1 approximation, in which the orbitals of the next atom in the periodic table (i.e. manganese, with occupations $1s(1)2s(2)2p(6)3s(2)3p(6)4s(1)3d(6)$, $\dots 4s(2)3d(5)$ and $\dots 4s(1)3d(5)$ respectively) were used for the chromium atom to model the partial relaxation of the system in the presence of the core hole.

In Fig. 2 we see the results of the calculations for the four final-state potentials and three program modes compared with the experimental spectrum "EX". This was taken at room temperature from a crystalline powder sample dispersed in a supporting medium. The first main peak, which we have arbitrarily set at energy zero, was measured to be at an X-ray energy of 443.35 Ry (6032.1 eV). The corresponding theoretical peaks have been aligned with it in energy (no theoretical total energy differences being available). The experimental edge has been normalized (in the absence of an absolute cross-section measurement) to the edge-jump of elemental chromium of 42.02 kb (1.501 mau). Each theoretical spectrum extends from the its continuum threshold up to four Rydbergs in photoelectron energy and is shifted vertically in the figure by some multiple of 1.5 mau. We have not tried to model any instrumental or core-hole lifetime broadening in the theoretical spectra.

We see that non-MT corrections are significant, the FP results (+IR mode) giving better energy positions for the spectral features and more cleanly reproducing the features below the first main peak (which are bound-state transitions appearing in the continuum because our potentials are not self-consistent). However, there is still some difference between theory and experiment even in the FP case. The average magnitude and gross features of all theoretical spectra are about right, but the size of the oscillations is generally too large by a factor of two to three. Consequently, we must conclude that other aspects of the physical model are important in the XANES region; particularly inelastic loss, self-consistency and exchange-correlation, which are missing or badly treated. The $L = 0$ and $+L > 0$ modes seem quite uniform by comparison with the +IR mode indicating that the MT approximation hides an underlying sensitivity to the way in which we construct the potential of the final state. Presumably we need self-consistent electron densities and perhaps some treatment of the dynamical behaviour of the core hole. While we cannot make detailed wide-ranging conclusions on the basis of results for a single system, it is at least clear that much work remains to be done on the physical model of XANES before obtaining close agreement with experiment.

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