A screened static-exchange potential for core electron excitations

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Abstract

We explore the use of a screened potential for static exchange calculations of core electron excitations, and to which extent this potential can relieve the main limitation of the static exchange method, namely the non-account of the residual screening in the presence of the excited electron. The screened potential is obtained by projecting the target state on a set of polarized orbitals, giving origin to a fully screened potential. Applications are presented and discussed for X-ray absorption spectra of a set of molecules of different size and type. It is found that with the little extra computational effort using the screened potential, the low-energy part of the spectra is generally improved, while the error in the term values are roughly of equal magnitude but of different sign compared to the normal static-exchange calculation. Various aspects of the screened and un-screened static-exchange approximations are analyzed in comparison with other techniques. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The presently available ab initio strategies for calculations of molecular electronic spectra can be roughly divided into separate state methods and Green's function – or propagator – methods. The former are more or less straightforward extensions to excited states of techniques for calculations of ground state energies and wave functions, while in the propagator methods the excitation energies and transition probabilities are computed directly. Some of these methods can give accurate results taking into account a significant part of the electron correlation, but their practical application is then often limited to the description of either small systems and/or of a restricted number of excited states in the spectrum. For large molecular systems and for the description of the electronic spectrum over a large energy range, covering both the discrete and the continuum excited states, one has to resort to less sophisticated ab initio methods that give a simplified but more complete view of the electronic excitation processes. Other categories of methods, like the MS Xα method [1–3], and those based on density functional theory [4,5] should also be mentioned as viable alternatives in this context.

Among the simpler ab initio approaches the static-exchange (STEX) approximation [6] is

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probably the one that has been more extensively applied to the calculation of different molecular electronic spectra. It is, in one sense, the lowest order in a hierarchy of propagator methods, but can also be viewed as a separate state approach in which the excited state is simply approximated by the coupling of a target ionic state and an excited orbital optimized in the (static) field of the ion. This approximation can be considered physically well suited to describe core electron excitations as will be discussed in the following. It has for this purpose been implemented at the Hartree–Fock level in a direct double basis set fashion, with algorithms that can be efficiently used for large molecular species and very large basis sets [7,8].

Apart for electron correlation effects that eventually can be reduced to those between the target and the excited electron, the main error in the STEX method refers to the residual relaxation of the bound electrons due to the screening of the excited electron. STEX is then evidently more suitable for excited states that are reasonably described by "single excitations" and, among those, for high energy excited states of Rydberg or continuum character. For the lowest excited states, of valence character (either "discrete" or "shape resonance") the missing screening can instead lead to energy errors, which for core excitations of π^* character are in the range of 1–2 eV.

In the present work we investigate a simple modification of the static-exchange potential that can be effective in the short range around the excitation site, while retaining the correct Coulomb asymptotic behavior for the potential tail. In such a way the change in the potential affects sensibly only the excited states more localized in the molecular region (resonances both of discrete and continuum character). The resulting spectrum appears in most cases in better agreement with the experiment when compared to the standard STEX spectrum. A few applications of this polarized or "screened" potential will be presented and discussed for the X-ray absorption spectra (NEXAFS) of the following set of molecules: carbon monoxide, butadiene, hexatriene, benzene, pyridine, aniline and imidazole.

2. Method and computations

2.1. The static-exchange approximation

We assume, for simplicity, that the molecular ground state is a closed shell. The (singlet) excited state Ψ_i^N will be approximated by the antisymmetrized product of the (target) ionic state Ψ_j^{N-1} and the excited orbital ψ_v, in short notation,

$$\Psi_i^N \simeq \tfrac{1}{\sqrt{2}}(\hat{a}_{v_\beta}^+ \Psi_{j_\alpha}^{N-1} - \hat{a}_{v_\alpha}^+ \Psi_{j_\beta}^{N-1}) = \Psi_j^{N-1}[\psi_v], \qquad (1)$$

and the excitation energy will be given by $E_j^{N-1} + \epsilon_v - E_0^N$.

Keeping the ionic state Ψ_j^{N-1} frozen, the excited orbital ψ_v is optimized by requiring that the wave function in Eq. (1) satisfies the projected Schrödinger equation

$$\langle \Psi_j^{N-1}[\delta\psi_v] \mid \hat{H}_{\text{el.}}^N - E \mid \Psi_j^{N-1}[\psi_v]\rangle = 0 \qquad (2)$$

for all possible variations of the orbital ψ_v. The variational problem is then reduced to a one-electron Schrödinger equation with a potential including Coulomb and exchange-like terms depending on the one-electron density matrix of the ionic state; see for instance Ref. [9] where the Dyson amplitudes from a Green's function calculation were employed. Practical expressions for the potential in the more general framework of a multi-channel wave function have also been derived for a CI approximation of the ionic state [10,11].

However, in the most usual meaning of STEX, the ionic state in Eq. (1) is intended to be approximated at the SCF (one-determinant self-consistent field-) level for which the STEX Hamiltonian takes the form

$$\hat{h}_j = \hat{F} - \hat{J}_j + 2\hat{K}_j$$
$$= \hat{T} + \hat{V}_{\text{nuc}} + \sum_{i \neq j}(2\hat{J}_i - \hat{K}_i) + \hat{J}_j + \hat{K}_j, \qquad (3)$$

where $\hat{F}$, $\hat{J}_j$ and $\hat{K}_j$ are the standard Fock, Coulomb and exchange operators, respectively, and the index j now refers to the bound orbital from which the excitation occurs. The simple expression in Eq. (3) is valid in the case of a singlet ground state and no degeneracy of the orbital j. In the case

of excitations from a degenerate occupied orbital to a degenerate virtual orbital proper combinations of degenerate spin adapted determinants are required to obtain the correct spatial symmetry of the excited state and the STEX Hamiltonian for the calculation of the virtual orbitals then includes extra exchange-like terms. Explicit formulas for the cases of molecular symmetry C_{3v} and $C_{\infty v}$ can be found, for instance, in Refs. [12,13]. The same is true for excitations from open shell systems [14] where the presence of more than two open shells leads to different potentials for different spin coupling schemes.

In its basic form STEX is then characterized as an independent particle, independent channel, approximation based on the separation of the SCF ionic state and the excited orbital and is as such more suitable for spectra where "singly" excited states are dominating. Despite its limitations, STEX has been largely, and often successfully, applied to the overall description of electronic absorption spectra including both discrete and continuum energy regions. In fact the resolution of the one-electron Schrödinger equation

$$\hat{h}_j \psi_v = \epsilon_v \psi_v \qquad (4)$$

leads to a set of negative eigenvalues, converging to the ionization threshold, that represents true discrete states for the first valence channel or "quasi-discrete" states for inner valence and core channels. However, the STEX equation can also be solved for positive eigenvalues corresponding to electronic continuum states from which information on photoionization and scattering processes can be derived [15].

2.2. NEXAFS spectra

The independent channel approximation, implicitly assumed in STEX, is not completely satisfactory for valence shell excitations and is actually better justified from the physical point of view for processes involving core electron excitations in molecules because of the large energy separation of core levels of different elements and the generally large spatial separation of core orbitals on different atoms of the same species (chemically

shifted atoms). Moreover, the independent channel single-excitation approach can be easily implemented in terms of relaxed occupied orbitals optimized for the specific (core-hole) channel considered. This means that the ionic state is not anymore approximated at the Koopmans level, but it is optimized by a separate SCF calculation. This is relevant not only for the absolute values of the excitation energy of the main resonances, but also for their relative intensities. The static-exchange approach is, for the reasons just outlined, one of our choice for the study of processes involving the excitation/de-excitation of core electrons in large molecular systems and in particular for the calculation of X-ray absorption spectra (NEXAFS) [16].

The eigenvalue problem of Eq. (4) is solved by a projection on a basis set, orthogonalized to the occupied orbitals, that is particularly large in order to cover a wide energy range of the electronic spectrum. The extension of the basis sets employed and of the molecular systems that we intend to investigate calls for a direct SCF technique for the construction of the STEX Hamiltonian that is seen as a modified Fock Hamiltonian (Eq. (3)) with the correction transferred to the density matrices [7]. The direct calculation of the STEX Hamiltonian allows to take advantage of all the usual positive features of such an approach (density screening, symmetry, parallelism, etc.) and the computational work becomes equivalent to one direct SCF iteration.

2.3. Screened static-exchange potential

According to the approximation of separation between target (ion) and excited electron, the excitation energy to the final state in STEX is given by

$$E_{jv}^N = E_j^{N-1} + \epsilon_v - E_0^N = \mathrm{IP}_j + \epsilon_v. \qquad (5)$$

It is well known that Koopmans theorem gives a reasonable approximation of the valence shell ionization potentials (IPs), while for core ionization the difference with experiment is higher than 10 eV already for light atoms like C, N, O, F, owing to the substantial electronic relaxation

around the core hole. The rearrangement of the electron distribution after removal of a core electron is well described at the independent particle level by a specific SCF calculation for the hole state. The resulting IP (ΔSCF) shows deviations from the experiment that are typically in the range 1–2 eV and reproduces fairly well the dependence from the local electronic environment (chemical shift) observed for non-equivalent atoms of the same kind. The effect of electronic relaxation is relevant not only from the energetical point of view (leading to a strong shift of the X-ray absorption spectra) but also for the actual electron distribution in the ionic state. This is shown in Fig. 1 by a comparison of the NEXAFS spectrum of CO computed by adopting the frozen (gs) orbitals and the relaxed (ion) orbitals for the calculation of the STEX potential vs the experimental spectra at the C- and O K-edges. Except for the (many-electron) fine-structure superposed on the near-edge continuum that, of course, cannot be simulated by STEX that is an independent particle approximation, the features of the experimental

carbon NEXAFS spectrum are evidently much better reproduced by the STEX calculation using the relaxed orbitals. However, the strong first discrete peak and the shape resonance in the continuum are shifted to higher energy, about 2 and 5 eV respectively. Considering that the ΔSCF IP is 1.3 eV from the experimental value, the computed spectral profile looks in some way compressed in the region below the ionization threshold. This reduced energy range for the negative term values indicates a too low attractive character of the STEX potential and can be traced to an "overrelaxation" around the bare core hole in the absence of the excited electron. A possible way of correcting the STEX eigenspectrum could be based on a perturbative approach taking into account, at least to first order, the screening potential due to the excited/ionized electron that is missing in the STEX approximation. However, a standard perturbative procedure applied to each excited state would be rather cumbersome and also not well justified for STEX eigenstates belonging to the continuum, where the intra-channel coupling be-
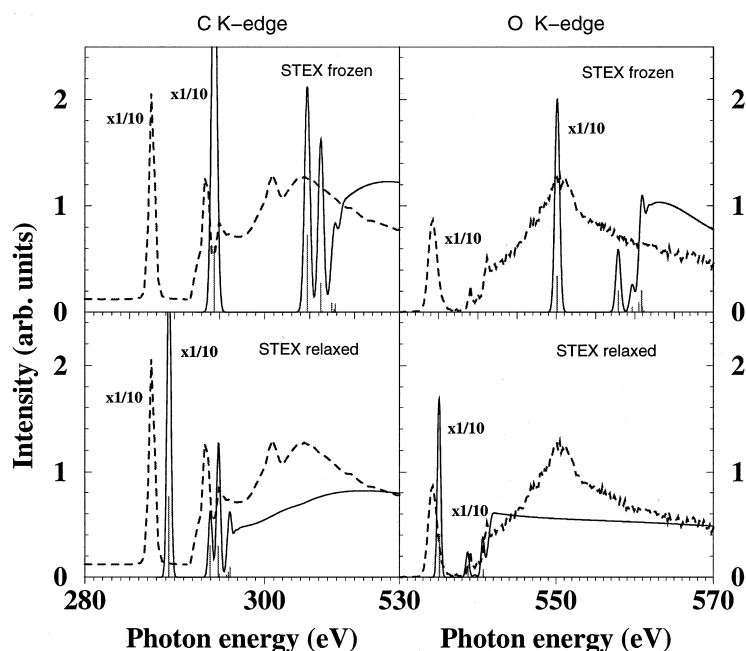

Fig. 1. Carbon and oxygen 1s NEXAFS spectra of the carbon monoxide molecule calculated using relaxed ion and frozen ion STEX approaches (the computed IPs are C 1s: 297.41 eV, O 1s: 542.08 eV). The experimental spectra [28] are given by dashed lines.

tween continuum states introduced by the perturbation potential should be correctly treated by a scattering procedure. Moreover, a separate perturbative correction of each excited state would not lead, in general, to mutual orthogonality and the excited states would lose the spectroscopic character of the STEX states.

In order to maintain the conceptual and practical advantages of the STEX approach, where the full spectrum derives from the same potential, we have chosen the way of transforming such a potential from that derived from the electron distribution of the target in the ionic state, to that corresponding to the electron distribution of the lowest core excited state having valence character and strong intensity. For the majority of molecules we have investigated, such a core excited state is easily identified as the π^* state, but can also be other screening valence states like σ^* states. The procedure to compute the "screened" potential then consists of a small open shell SCF calculation for the first core excited state described at the simplest level of a single excitation from the core orbital to the lowest unoccupied orbital (LUMO). Such a calculation supplies both a ΔSCF approximation of the excitation energy to the LUMO and a set of (singly and doubly) occupied orbitals. With the exception of the LUMO, this set of orbitals are considered to represent the electronic distribution of a "screened" ionic state and are used, by employing the standard formulas and algorithms for the STEX procedure, to compute the "screened" STEX potential. The eigenvalues of the "screened" STEX potential are then added to the ΔSCF IP to obtain the excitation energies.

2.4. Computational details

The energies of the ground and core-ionized states were calculated at the Hartree–Fock level, using the norm-extended quadratically convergent SCF [17,18] method. This technique allows to avoid a variational collapse during the optimization of the core-ionized and excited states by a two-step procedure in which an intermediate optimization with the core orbital frozen is followed by a straight Newton–Raphson step of optimiza-

tion of the wave function in the local quadratically convergent region [18].

Simulations of the NEXAFS spectra have been performed using the STEX approximation in ordinary and screened potential forms discussed in the subsections above, using well tested parameterizations. The double basis set technique was thus employed, using a valence triple zeta [19] basis set with one polarizing d-function (pVTZ) for the calculations of the bound molecular orbitals in the SCF and ΔSCF optimizations and expanding this relatively small basis set by an additional augmented non-redundant basis set which consists of a large set of diffuse basis functions (20s, 18p, 20d) centered at the core excitation site.

For simulations of the continuum part of the spectra the Stieltjes imaging technique [20,21] has been employed. The computed spectra were then convoluted with a Gaussian function of arbitrary but reasonable linewidth in order to simulate the effect of both the limited photon resolution and the vibrational broadening of the bands in the discrete energy region, thus making the comparison with the experimental data easier.

3. Results

3.1. CO

In order to illustrate the main difference between the polarized (screened) and un-polarized levels of the STEX approximation, we first consider the NEXAFS spectra at the C and O K-edges of CO. A comparison of theoretical and experimental results is reported in Fig. 2.

The large differences between frozen and relaxed results have already been pointed out in the previous section. The main differences between the "relaxed" and "screened" spectra are found in the positions of the resonances with valence character (π^* and σ^*), as one might expect. The effect of the "screened" potential on the excited states of Rydberg character is negligible, as it should be due to their limited penetration in the core region. It is evident that the position of the strong first peak (π^*) in the carbon spectrum is shifted to higher
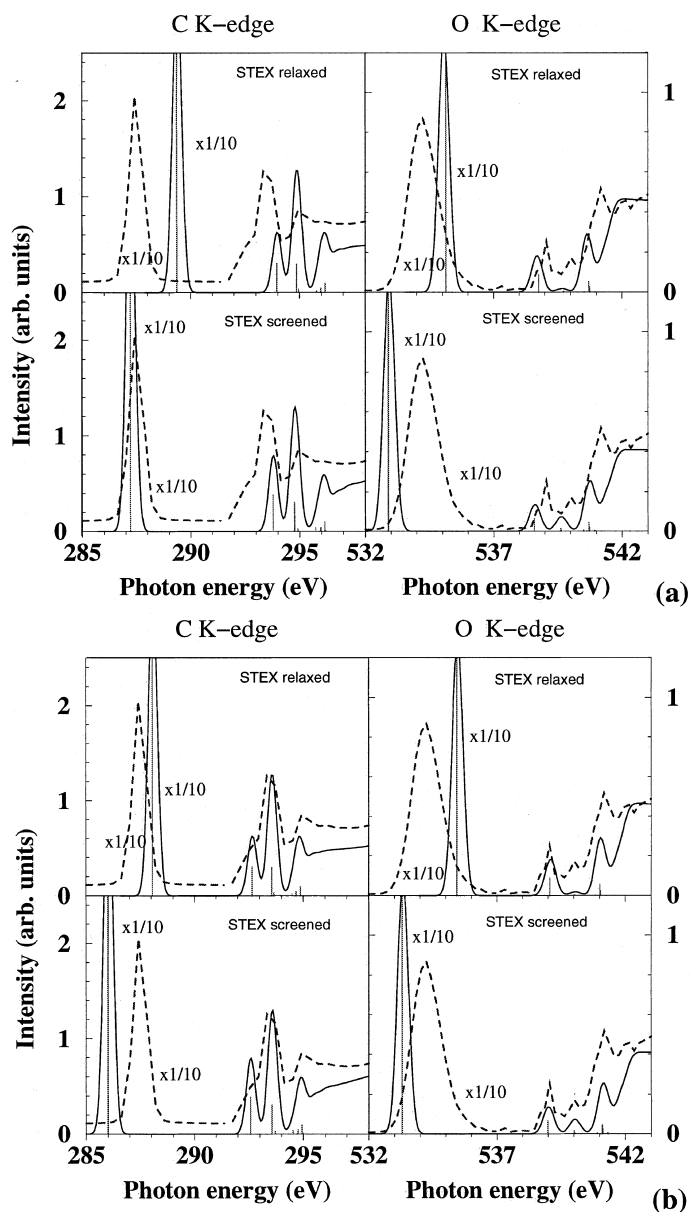
Fig. 2. Carbon and oxygen 1s NEXAFS spectra of the carbon monoxide molecule calculated using relaxed ion and screened ion STEX approaches. The experimental spectra [28] are given by dashed lines: (a) using the computed IPs (C 1s: 297.41 eV, O 1s: 542.08 eV) for the plot of the simulated spectra, (b) using the experimental IPs (C 1s: 296.14 eV, O 1s: 542.47 eV) for the plot of the simulated spectra.

energy by almost 2 eV, while the screened spectrum is in better agreement (Fig. 2a). However, the improvement is only apparent in the sense that the computed IP is 1.3 eV too high. Re-normalizing the spectra to the experimental IP, see Fig. 2b, a

different picture emerges, now the screened value becomes significantly too low. A comparison of the term values (IP-π^* energy) offers a more "fair" comparison. For the C 1s–π^* energies these are 8.11, 10.21, 8.68 eV using the relaxed, screened and

experimental data, respectively. For the O 1s–π^* energies the corresponding term values are 6.98, 9.08, 7.87 eV. Thus, although the absolute C 1s–π^* peak energy is better in the screened approach, the term value is about as poor (or good), giving instead a too wide NEXAFS spectrum. The reduced energy range for the term values in the "ion-STEX" case with a too low attractive character of the STEX potential and an overrelaxation around the bare core hole in the absence of the excited electron is converted in the "screened-STEX" case to an underestimation of the relaxation around the core hole of the bound electrons and a potential of too attractive character and therefore to term values that are too large.

3.2. Larger molecules

We have tested the "screened-STEX" approach for a set of somewhat larger molecules and compared it to the "ion-STEX" results and to experiment. The *trans*-butadiene-1,3 NEXAFS spectrum is first in line, see Fig. 3. In comparison with experiment [22,23] we see that the screened-STEX results for the low C 1s–π^* excitations improve on the ion-STEX results; the former seem to be 1 eV too low while the latter are 2 eV too high. One
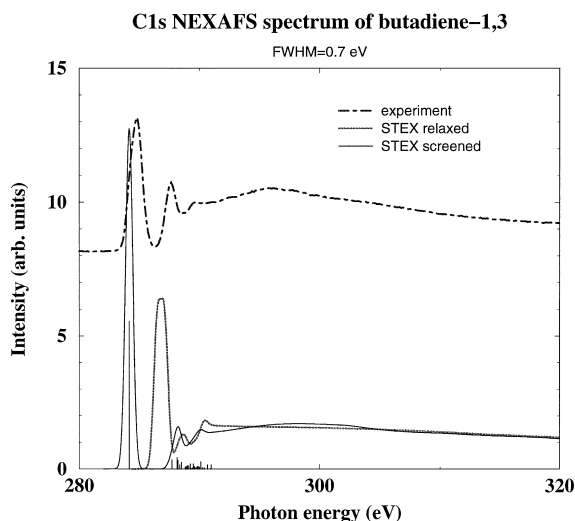

C1s NEXAFS spectrum of butadiene–1,3
FWHM=0.7 eV

Fig. 3. Calculated C 1s NEXAFS spectrum of *trans*-butadiene-1,3 using the relaxed ion and screened ion STEX methods. Experiment from Ref. [22].

notes though that the splitting (chemical shift) seems to collapse in the screened calculation at variance with experiment. Perhaps a more fair comparison is given in Table 1 by the term energy differences from the ΔSCF computed values of the $1s \rightarrow \pi^*$ transitions (shown in parentheses). They compare as 1.18 and 1.47 eV (ion-STEX) to -1.16 and -1.45 eV (screened-STEX), respectively, in the calculations utilizing the double basis set technique (see Table 1). The excitation energies calculated by ΔSCF are 285.30 and 285.61 eV for the end- and mid-carbons which can be compared with 284.5 and 284.9 eV measured experimentally. The absolute values obtained by screened-STEX are closer to experiment than even ΔSCF, but this improvement is in some sense lucky since the calculated carbon IP values are too high; the term values from the two approaches seem to hit experiment equally well (or bad) but from different sides. It is notable that the prediction of the weaker bands (largely σ resonances) higher up in the spectrum are quite similar for the two approaches. A vibronic analysis would further distinguish the assignment capability between these approaches.

We have also computed three carbon nitride molecules, which can show comparisons for both carbon and nitrogen spectra, see Figs. 4–6. The results for all three molecules are basically the same, the screened-STEX method gives a better comparison with experiment, in particular for the first strong π^*-like resonances. Again, though, the term values tell a somewhat different story.

The aniline N 1s spectra deserves a special comment, having apparently poor experimental spectra and poor theoretical assignments [24]. The latter is partly due to that multiple strong π and σ states mingle, in a quite unusual way, in a small interval of the first excitations. We see here that the screened-STEX shifts the positions of π but not the σ transitions so as to apparently shift only intensities and not energies in the spectra. The screened-STEX result gives so a significantly better (or more reliable) assignment, see Fig. 4b.

In Table 1 we have given ion-STEX and screened-STEX values for π^* excitation energies and compared them there with ΔSCF energies, which then form the "exact" reference for the two

Table 1
Comparison of the $1s^{-1}\pi^*$ excitation energies (eV) calculated by the ΔSCF, standard STEX and screened-STEX procedures

Atom	$E_{\Delta SCF}$ $1s^{-1}\pi^*$	E_{STEX} standard	E_{STEX} screened	IP ΔSCF
Benzene				
C	286.46	287.15(0.69)	285.49(−0.97)	290.51
Aniline				
C1	287.69	288.77(1.08)	287.23(−0.46)	291.77
C2	286.31	287.25(0.94)	285.68(−0.63)	289.96
C2′	286.31	287.25(0.94)	285.68(−0.63)	289.96
C3	286.23	287.27(1.04)	285.78(−0.45)	290.41
C3′	286.23	287.27(1.04)	285.78(−0.45)	290.41
C4	286.51	287.42(0.91)	285.89(−0.62)	289.77
N	403.66	402.36[a]	402.47[a]	405.30
Pyridine				
C1	286.62	287.69(1.07)	286.15(−0.47)	291.71
C1′	286.62	287.69(1.07)	286.15(−0.47)	291.71
C2	286.17	287.13(0.96)	285.67(−0.50)	290.83
C2′	286.17	287.13(0.96)	285.67(−0.50)	290.83
C3	286.04	287.11(1.07)	285.63(−0.41)	291.36
N	399.46	400.43(0.97)	399.00(−0.46)	404.68
Imidazole				
C1	287.97	289.26(1.29)	287.02(−0.95)	292.51
C2	287.18	288.48(1.30)	285.97(−1.21)	291.05
C3	287.56	288.65(1.09)	286.78(−0.78)	291.47
N1	400.22	401.59(1.37)	398.86(−1.36)	404.37
N2	403.16	403.61(0.45)	402.24(−0.92)	406.78
trans-Butadiene-1,3				
C1	285.30	286.48(1.18)	284.14(−1.16)	290.28
C2	285.61	287.08(1.47)	284.16(−1.45)	291.01
Hexatriene-1,3,5[b]				
C1	285.64	286.43(0.79)	283.07(−2.57)	289.97
C2	285.26	287.27(2.01)	284.89(−0.37)	290.90
C3	285.48	286.79(1.31)	284.11(−1.37)	290.45

Numbers in parentheses are the differences between STEX and ΔSCF energies.
[a] Energy of the lowest intensive transition which in fact is $N1s \rightarrow \sigma^*$.
[b] Computed without augmentation basis set.

methods. All three quantities refer to the same IP. It is seen clearly that ion-STEX overestimates excitation energies by 1–1.5 eV while screened-STEX underestimates them by the similar amount.

3.3. Discussion

3.3.1. Relation to other propagator approximations

The present results can be qualified by the nature of the STEX approximation in relation to other propagator approximations. We note that STEX is the lowest in this hierarchy of propagator methods, with a single particle excitation manifold but with the hole manifold truncated to one hole only, i.e. it is a single channel approximation. Having only one hole, the target state can be re-optimized for the particular hole state, and the particle excitations are determined with respect to that target (potential). This inherent possibility makes STEX useful for core excitations. Going up two levels of approximation we have the random phase approximation with single hole excitations (with many holes or channels) and single particle–hole de-excitations. These de-excitations often per-

turb the energy levels only to a small extent, but are important for two reasons; they ensure gauge invariance in the limit of a full basis set, which in turn makes oscillator strengths of "good" quality, and they partially introduce relaxation-correlation effects, then also, in a limited way, the screening of the target with respect to the excited particle. However, it should be added that just those important de-excitations in the operator manifold

C1s NEXAFS spectrum of aniline

FWHM=0.7 eV

N1s NEXAFS spectrum of aniline
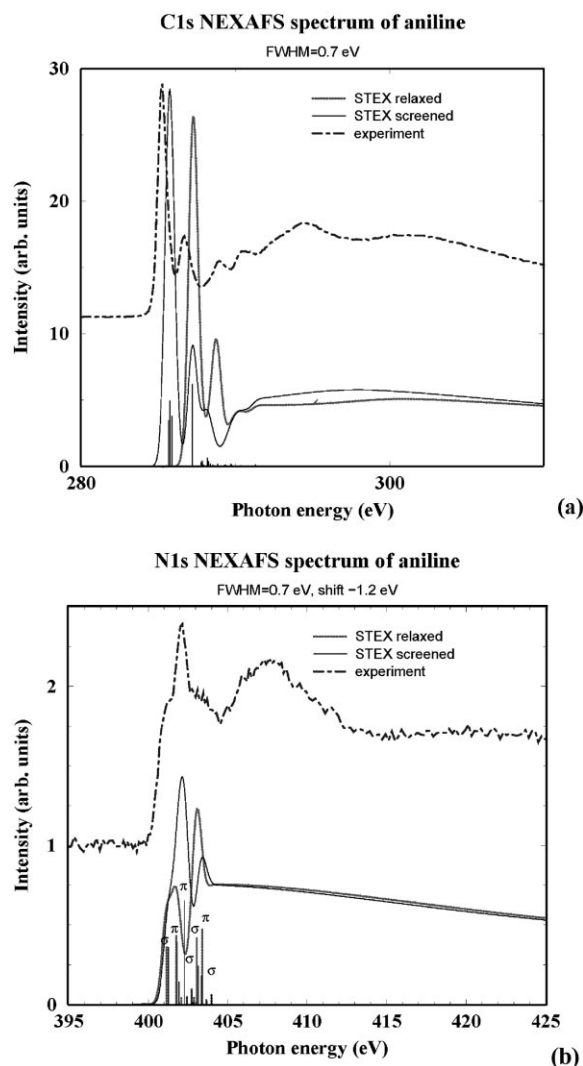
FWHM=0.7 eV, shift −1.2 eV

Fig. 4. Carbon (a) and nitrogen (b) K-shell NEXAFS spectra of aniline calculated using the relaxed ion and screened STEX approaches. Experiment from Ref. [29].
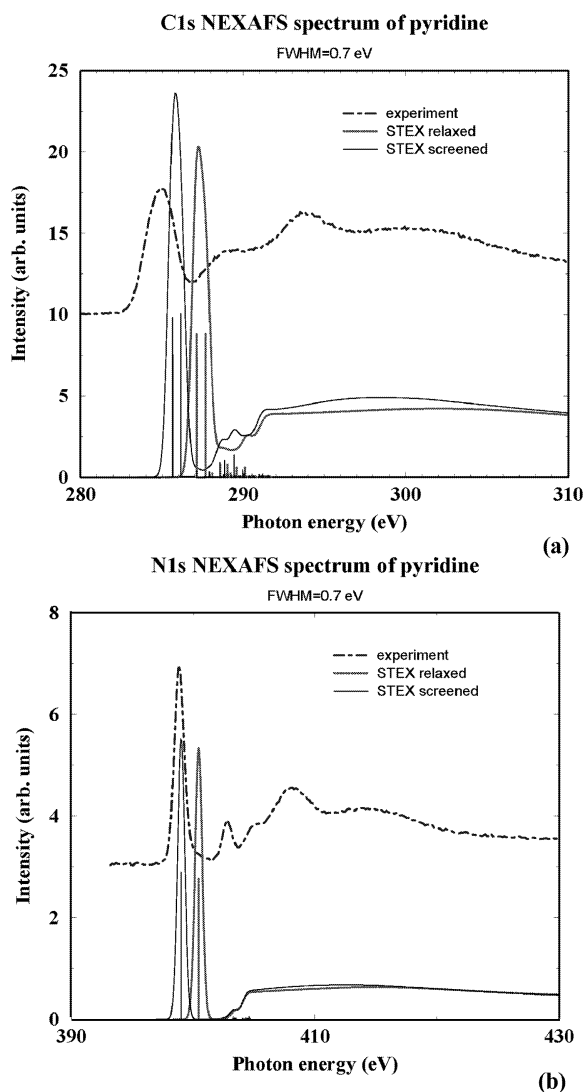
C1s NEXAFS spectrum of pyridine

FWHM=0.7 eV

(a)

N1s NEXAFS spectrum of pyridine

FWHM=0.7 eV

(b)

Fig. 5. Carbon (a) and nitrogen (b) K-shell NEXAFS spectra of pyridine calculated using the relaxed ion and screened STEX approaches. Experiment from Ref. [30].

which make the RPA method so useful in the optical/UV region make also this method unstable for core excitations, since one then must assume a non-relaxed ground state reference target, neglecting the most relevant physical effect in the excitation of core electrons. The level intermediate between STEX and RPA; the Tamm–Dancoff approximation, does not have the screening down-excitations and its multi-hole (multi-channel)

C1s NEXAFS spectrum of imidazole

FWHM=0.7 eV

(a)

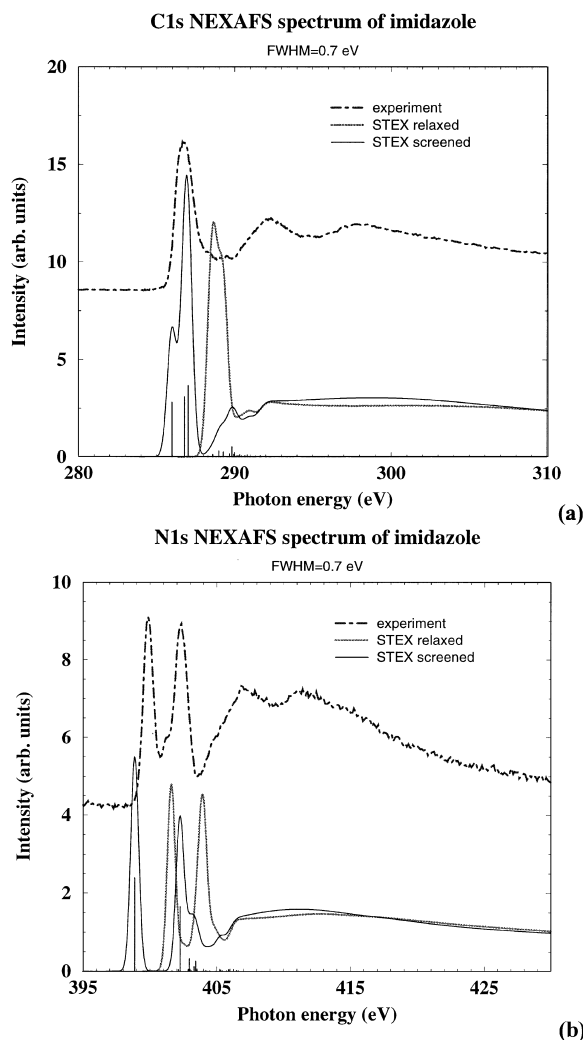## N1s NEXAFS spectrum of imidazole

FWHM=0.7 eV

(b)

Fig. 6. Carbon (a) and nitrogen (b) K-shell NEXAFS spectra of imidazole calculated using the relaxed ion and screened STEX approaches. Experiment from Ref. [31].

character makes it impossible to renormalize the target to a relaxed potential as in STEX; for core excitations this approximation level is probably not useful, except in special circumstances of degeneracy (for instance for core excitations involving p and d holes). At present we can thus not foresee an effective low-scaling "X-ray propagator" with screening built in. Higher order propagators like the *algebraic diagrammatic construction* scheme based on the Green's function formalism

(Cederbaum and coworkers) are probably useful for smaller species, but are of course not "effective" in the sense discussed above.

3.3.2. Fractionally occupied core holes

Another way to manipulate the amount of target screening is to apply a fractional core hole. In fact, within the framework of density functional theory a transition potential with half an electron hole charge has been shown to yield very precise core excitation energies to valence-like levels [4,5]. The excitation energies with the fractional hole approach are though derived in a different way; the good results for the lowest excitation are due to the fact that half an electron corresponds to the best (cubic) approximation to the SCF energy of the first excited state [25], but the potential with half an electron is not "correct" for the remaining Rydberg and continuum states nor for the asymptotic behavior.

3.3.3. Valence–Rydberg mixing

The existence of core-excited states with mixed valence–Rydberg character seems to be quite common as revealed in many recent NEXAFS studies [26]. The effect of using an unscreened or a screened potential optimized for the bare core hole state, respectively, a particular core-excited state, is less clearcut when there is strong valence–Rydberg mixing which distributes the valence character into several states, and thus when there is no single state with strong core screening.

Kosugi et al. [26,27] implement a technique that bear resemblance to the presently adopted method, i.e. optimizing a σ^* state using orbitals from this state to construct the potential. They separate the treatment of valence σ^* states and of Rydberg states, the latter are obtained by a procedure in which they are orthogonalized to the σ^* orbital (projecting out this valence state before diagonalization). In the present work we allow all states belonging to a given channel to mix by constructing and diagonalizing the channel Hamiltonians without any constraint, except for orthogonalization to the occupied orbitals. As shown previously for the O_2 molecule [14] this makes some difference

in the computed NEXAFS spectra in the region with anticipated valence-Rydberg mixing.

3.3.4. State specific correlation

Rydberg (and non-resonant continuum-) electrons are not significantly perturbed by electron correlation with the ion core, while for valence states the excited electron in general correlates with the bound electrons. The screening discussed above is a mean-field, average, screening, which essentially leaves out the electron correlation obtainable in multi-electron expansions. Configuration interaction and multi-configuration SCF are multi-electron methods alternative to propagator methods and which take electron correlation into account in a state-specific way. Both the ion-STEX and screened-STEX results for valence states are subject to correlation errors in this sense, while the ion-STEX results for Rydberg/continuum electrons lead to a more essential experimental agreement compared to screened-STEX due to the absence of strong electron correlation with the ion core.

4. Conclusion

We have tested the notion of a screened ion approach to improve the performance of the STEX approximation for core–valence excitations. The study of results for a number of molecules leads us to the conclusion that an improvement indeed is obtained, although the screened ion results tend to overshoot to the other end with too little screening and too small excitation energies. Also some of the apparent improvement in the experimental comparison is due to the fact that the SCF value for the reference level, that is the IP, generally tends to be too high. If this improvement should be called "actual" or "apparent" is a little matter of taste since the screened-STEX method, although well defined, evidently contains cancellation of errors (between too low virtual orbital energies and too high ionization energies), which might not be systematic in terms of electron correlation. In any case, the combined use of the "ion-STEX" and the "screened-STEX" methods sets the limits of the STEX approach itself and prob-

ably so improves its utility in assigning X-ray absorption spectra near the edge.

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