Calculation of resonances in near-edge X-ray absorption fine structure spectra using the constant chemical potential local density approximation method

V.L. Shneerson, D.K. Saldin, W.T. Tysoe *

Departments of Chemistry and Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

Received 6 June 1995; accepted for publication 7 August 1995

Abstract

Known prescriptions for the implementation of exchange and correlation potentials fail to reproduce the near-edge X-ray absorption fine structure (NEXAFS) spectrum for a test case of a gas-phase acetylene molecule using computer simulations. A new constant chemical potential-local density approximation (CCP-LDA) calculation method has been developed which ensures the constancy of the chemical potential throughout the molecule for which the calculation is performed within the framework of the local density approximation. A Hedin–Lundqvist potential is used to represent the exchange and correlation potential of the excited state. This method provides excellent agreement between theory and experiment for a range of small gas-phase molecules including acetylene, carbon monoxide, nitrogen and oxygen.

Keywords: Alkenes; Alkynes; Carbon monoxide; Computer simulations; Near-edge extended X-ray absorption fine structure (NEXAFS); Nitrogen; Oxygen

1. Introduction

X-ray absorption techniques, in which electron transitions from core levels into states above the vacuum or Fermi level are excited, have proven extremely useful in determining the short-range order of both the bulk phase as well as surface species. The oscillation of the X-ray absorption coefficient above the energy thresholds for the excitation of core electrons is formally divided into the so-called NEXAFS (near-edge X-ray absorption fine structure) region, which refers to the parts

of the absorption spectra up to about 50 eV from an absorption edge, and EXAFS (extended X-ray absorption fine structure) for the parts of the spectra more distant from the edge. In both regimes, oscillations are found in the absorption cross section which originate from a modification of the photoelectron final state by the backscattering of the ejected photoelectron. The formal division between the two regimes arises since, for electrons ejected from the atomic cores with relatively high energies, the atomic scattering factor exhibits a strong maximum in the forward direction so that the X-ray absorption coefficient as a function of energy is dominated by single-scattering processes. This significantly simplifies the analysis

---

* Corresponding author. Fax: +1 414 229 5530; E-mail wtt@alpha2.csd.uwm.edu.

of the spectra. However, the structural information that can be extracted from this experiment is limited to atomic radial distribution functions. In contrast, in the NEXAFS regime ($E_K < 50$ eV), multiple scattering predominates, so that analysis of these spectra can yield much more structural information, for example, the coordination geometry, molecular orientations, and the density and symmetry of unoccupied valence electron states. This also means, however, that all scattering processes must be taken into account to accurately describe the positions of the resonances in NEXAFS.

It has also been demonstrated that it is crucial to include exchange and correlation effects on the dynamics of the ejected core electron in the analysis of the NEXAFS spectra since the total energy E of an electron immersed in a sea of other electron may be written as:

$$E = K + V_H + V_{XC}, \tag{1}$$

where K is the kinetic energy, V_H its Hartree potential energy and V_{XC} its exchange and correlation energy. A complication implicit in the exchange–correlation potential is that it is also a function of the electron kinetic energy K. In the case of EXAFS, where K is relatively large, E_{XC} varies only slowly with K and is generally neglected. Nonetheless, Mustre de Leon et al. [1] have suggested that, even in this case, an energy-dependent exchange–correlation potential must be used for the excited final state, for the best quantitative agreement with experiment. The exchange–correlation energy, however, varies very strongly with kinetic energy for small values of K so that it becomes crucial to include its effect in calculating NEXAFS resonance energies. This strategy was used to successfully compare resonances for NEXAFS spectra of hydrocarbon intermediates in the trimerization of acetylene to benzene on Pd(111) [2]. In this case, exchange–correlation energies were included in a *post-hoc* fashion by correcting the kinetic energy scale using an analytic Dirac–Hara potential [3]. This rather simple expedient was, nevertheless, successful in correctly calculating the resonance positions and establishing the nature of the surface species. These results were important in emphasizing the necessity of including

these effects in the calculation. In the following, exchange–correlation effects are included in an *a priori* fashion using several model potentials for the exchange and correlation energy. It is found, however, that, irrespective of the type of model potential used, the resulting calculated value of the chemical potential of the electron varies as a function of position. This is an unphysical result. We therefore take as a constraint that any wavefunction calculated by including exchange and correlation effects must yield a spatially invariant chemical potential. Application of this method successfully predicts the positions of resonances in a number of small molecules, for example, acetylene, carbon monoxide, nitrogen and oxygen.

2. Multiple-scattering calculations of NEXAFS spectra

The spatial variation of the potential experienced by an electron immersed in a solid can be very complicated. A common representation that has proven very useful is the so-called muffin-tin model. This model has been extensively used in the calculation of the electronic structure of metals [4], and in the theoretical modelling of electron spectroscopies, such as photoemission [5] and X-ray absorption [6], as well as in calculating low-energy electron diffraction (LEED) intensities [7], as a function of electron energy. In this model, the potential near the atom core is taken to be spherically symmetric up to a critical radius known as the muffin-tin radius, and constant outside this region. The final-state wavefunctions for electrons in the sample can be calculated relatively straightforwardly using this potential. In NEXAFS, the effect of multiple scattering of the ejected core electron is taken into account in a small cluster around the emitting atom and where the cluster is divided into a series of concentric shells [6,8]. Since, for a large number of scatterers, computer algorithms for inter-shell multiple scattering tend to be more efficient than those for intra-shell scattering, a large number of atoms may be included in the cluster by this means. Multiple-scattering processes within each shell are included in turn, but due to inelastic damping, only those

electrons whose scattering paths are dominated by atoms in the nearest shells have a significant chance to be scattered back and of affecting the absorption rate. Thus, only a few shells need be included in the calculation to achieve good convergence. The absorption spectrum is then calculated as a function of the X-ray photon energy ω where:

$$\omega = E - E_C \qquad (2)$$

in Hartree atomic units, which are used throughout this paper, and E_C is the energy of the core electron and the total energy is specified by Eq. (1) so that:

$$\omega = K + V_H + V_{XC} - E_C. \qquad (3)$$

Thus NEXAFS peaks correspond to constructive interference in the multiple scattering of an ejected core electron within the neighborhood of the absorbing atom, and their energies are determined by the wavelength (or kinetic energy) of the outgoing electron.

The exact form of the exchange–correlation energy is not known, although a number of approximations to this value are available. An early calculation of the corresponding potential was made by Dirac [9] and first used to analyze electron spectra by Hara [3]. This potential is calculated using the Hartree–Fock approximation to a many-electron state by assuming that the positive charges of the atomic nuclei are uniformly distributed (the jellium model). This potential was used as an energy correction scale in previous calculations [2].

More recently, Hedin and Lundqvist [10] have introduced a potential that is characterized by a strong energy dependence, which also includes an imaginary part caused by the creation of electron–hole pairs and plasmons. Other forms of exchange–correlation potentials have been proposed by other authors [11–13].

One of the key problems in the calculation of X-ray absorption spectra is to determine the threshold for photon absorption, in order to establish the position of the absorption edge. This threshold has been identified with the chemical potential, μ, of the interstitial region between the muffin-tin spheres representing the atoms. Thus, if an electron is excited to some energy above the chemical potential in an interstitial region of the

local electron density $n_{int}(r)$, its total potential energy V_{int} may be written as:

$$V_{int} = \langle V_{gr}(n_{int}(r)) \rangle + \langle \delta V_{XC}(E, n_{int}(r)) \rangle, \qquad (4)$$

where $\delta V_{XC}(E, n_{int})$ is the energy-dependent part of the exchange–correlation potential above the Fermi level and V_{gr} is the ground state potential which includes the ground state exchange–correlation energy. This constant interstitial muffin-tin potential (the so-called muffin-tin zero) serves as a reference level and is determined according to Eq. (4) as an average of the potentials outside the muffin-tin spheres. Thus, the kinetic energy of an excited electron in the interstitial region, where the potential is constant as a function of position, is given by:

$$k(E)^2/2 = \langle k_F^2(n_{int}(r))/2 \rangle + E - \langle \delta V_{XC}(E, n_{int}(r)) \rangle, \qquad (5)$$

where $k(E)$ is the energy-dependent wavevector in the interstitial region and the total electron energy is measured with respect to the chemical potential μ:

$$\mu = \langle k_F^2(n_{int}(r))/2 \rangle + \langle V_{gr}(n_{int}(r)) \rangle. \qquad (6)$$

This equation is generally extended also to the region within the muffin-tin.

3. Calculations of NEXAFS spectra by prior prescriptions: inclusion of exchange and correlation effects

The simple muffin-tin model of an artificial crystal of repeating units of acetylene (C_2H_2) was used to calculate a NEXAFS spectrum. In order to approximate the potential of the gas-phase acetylene within the constraints of a muffin-tin model, the space between each molecular unit was increased until no discernable changes were observed in calculated X-ray absorption spectra. The ground state exchange energy was represented by the Slater $X\alpha$-potential [13].

The results of the calculation are shown in Fig. 1 for the carbon K-edge NEXAFS of gas-phase acetylene. Exchange–correlation effects in the excited state were included using either Dirac–
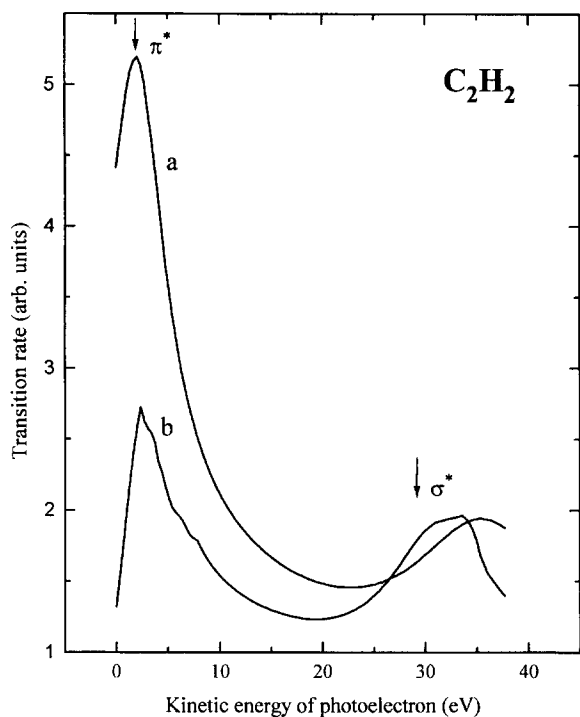
Fig. 1. Computer simulation for C K-shell NEXAFS spectrum of gas-phase acetylene molecule using different prior prescriptions for the exchange-correlation energy. Spectrum (a): Assuming the Dirac–Hara potential; spectrum (b) from the Hedin–Lundqvist potential with either of them implemented using the LDA scheme of Ref. [1]. Experimentally measured positions of the π^* and σ^* resonances are indicated by arrows.

Fig. 2. Radial variation of the chemical potential μ within the C muffin-tin, using our model, of an acetylene (C_2H_2) molecule. Line (a): that calculated with both potential and kinetic energy estimated within the LDA. A discontinuity occurs at the muffin-tin radius of ~ 1.1 a.u., beyond which μ takes the value indicated by line (b), the corresponding estimate for the interstitial region.

Hara (curve a), or Hedin–Lundqvist (curve b) potential. In both cases the agreement with the experimental positions of NEXAFS spectrum [15], which are indicated by arrows, is poor.

The reason for this disagreement is the neglect of the physical requirement that the chemical potential should remain constant throughout the system. To illustrate this point, the resulting variation of $\mu(r)$ (the chemical potential) within a carbon atom muffin-tin sphere of the artificial acetylene crystal is depicted in Fig. 2. This "chemical potential" becomes more and more negative as r decreases so that it is obvious that the method does not ensure the constancy of the chemical potential. Such a behavior is a consequence of the partitioning of the potential field in the muffin-tin model. The averaging of the interstitial field itself does not guarantee the appropriate behavior of
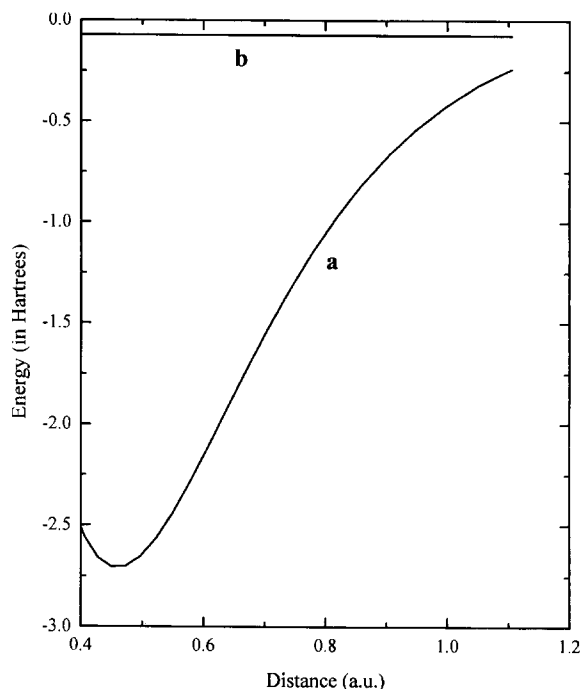
physical values inside the muffin-tin. A direct connection between these two regions of space may be made through the law of conservation of energy.

4. Present calculations of NEXAFS spectra: the constant chemical potential method

In order to ensure that the chemical potential remain constant throughout the system, the local density relation

$$k_F(n(r)) \propto n^{1/3}(r), \tag{7}$$

should be replaced by the energy conservation law:

$$k_F(r) = [2(\mu - V_{gr}(r))]^{1/2}. \tag{8}$$

This substitution will also effect the value of the local kinetic energy $k^2(r)/2$ of a photoelectron

within the muffin-tin spheres and, through it, its multiple scattering from these muffin tins [16].

The NEXAFS spectrum for acetylene is therefore recalculated, but now insisting that the chemical potential is kept constant as a function of position, both inside and outside the muffin-tin. The results are shown in Fig. 3. With exchange–correlation effects in the excited state calculated using a Hedin–Lundqvist potential, the relative positions of the spectral peaks agree very well with the experimental ones, indicated by arrows on Fig. 3. It should be emphasized that the calculation involves no adjustable parameters. In addition, both the relative peak intensities and the relative widths of the π^* and the σ^* resonances are in good agreement with the experimental spectra. The π^* resonance is narrow because it is more similar to its original ion-core states than the σ^*-resonance to its constituent atomic states, due to the different degree of overlap of the original atomic states. In all the calculations reported, we took the imaginary part

of the potential to be 1 eV in order to simulate a typical experimental resolution.

In order to establish whether the method has general applicability for a range of small molecules, the CCP-LDA method was used to calculate the location of resonances for a number of homonuclear or heteronuclear diatomic molecules as well as for ethylene. The results are summarized in Fig. 4 for CO and C_2H_4 and in Fig. 5 for N_2 and O_2. The experimental position of the π^* and the σ^* resonances [15,17] are again indicated by vertical arrows and, in all cases the calculated peak positions agree very well with the experimental values.

5. Conclusions

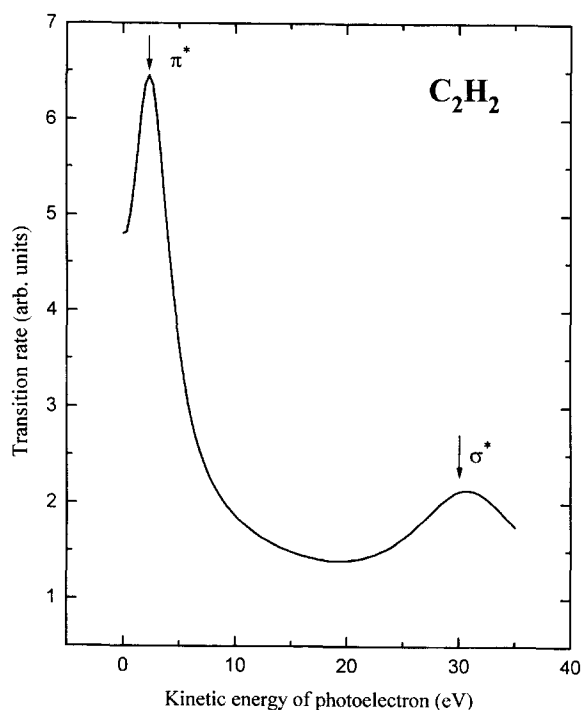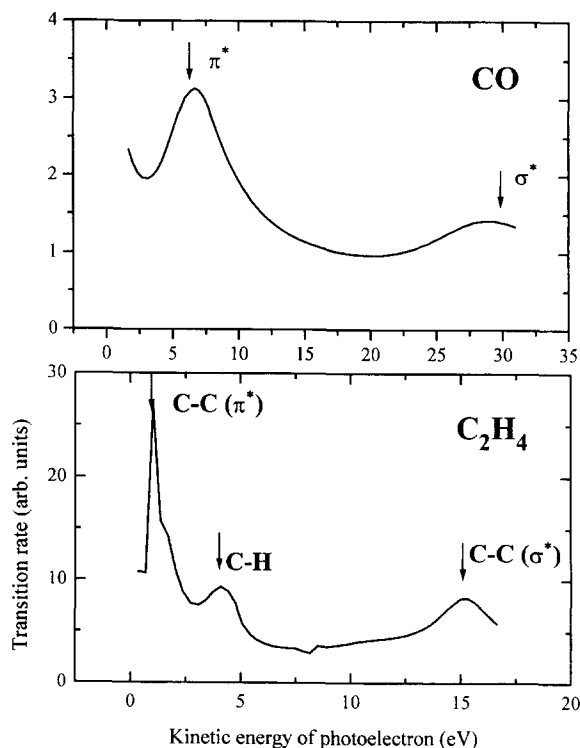The energy dependence of the exchange correlation potential for a core electron excited by an

Fig. 3. Computer simulation of the carbon K-shell NEXAFS of gas-phase acetylene by the CCP-LDA method. Experimentally measured positions of the π^* and σ^* resonances are indicated by arrows.

Fig. 4. Computer simulation of the carbon K-shell NEXAFS of gas-phase carbon monoxide (CO) and ethylene (C_2H_4) by the CCP-LDA method. Experimentally measured positions of the π^* and σ^* resonances are indicated by arrows.
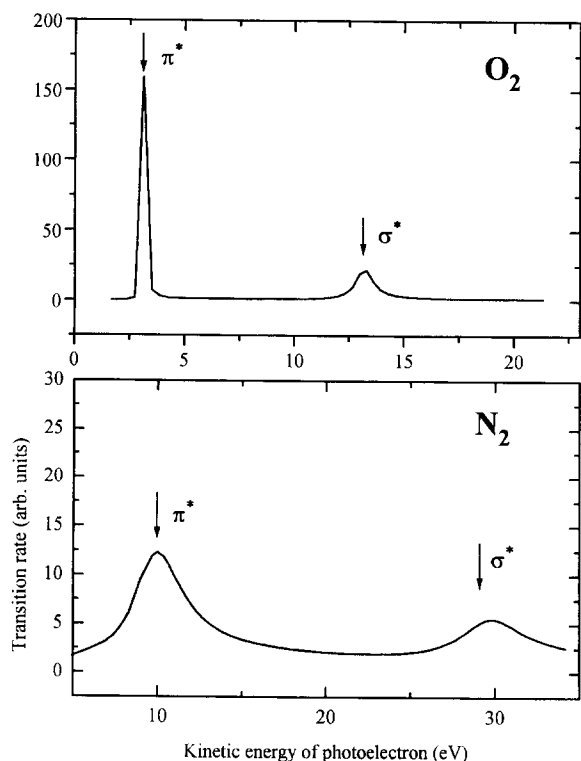
Fig. 5. Computer simulation of the carbon K-shell NEXAFS of gas-phase oxygen (O₂) and nitrogen (N₂) by the CCP-LDA method. Experimentally measured positions of the π* and σ* resonances are indicated by arrows.

X-ray photon is significant for arriving at correct structural conclusions from calculations of NEXAFS spectra. We have illustrated this point using some common exchange and correlation potentials such as a Slater $X\alpha$ potential, a Dirac–Hara potential, and the Hedin–Lundqvist potential for the K-edge excitation of the gas-phase acetylene molecule. Each of these yield different calculated peak positions, none of which agree well with experiment. In order to overcome this problem, we have developed a new constant chemical potential-local density approximation (CCP-LDA) method [16], which is based on the physically reasonable idea that the chemical potential should remain constant throughout the region surrounding the absorbing atom. Implementation of the model, using a Hedin–Lundqvist potential, yields excellent agreement with the experimental data.

In order to verify that the CCP-LDA model is equally applicable to other systems, we have applied the model to other small molecules and obtain excellent agreement between the calculated and experimental NEXAFS spectra of gas-phase carbon monoxide, ethylene, oxygen and nitrogen.

Acknowledgements

References

[1] J. Mustre de Leon, J.J. Rehr and S.I. Zabinsky, Phys. Rev. B 44 (1991) 4166.
[2] H. Hoffmann, F. Zaera, R.M. Ormerod, R.M. Lambert, J.M. Yao, D.K. Saldin, L.P. Wang, D.W. Bennett and W.T. Tysoe, Surf. Sci. 268 (1992) 1.
[3] S. Hara, J. Phys. Soc. Jpn. 22 (1967) 710.
[4] V.L. Moruzzi, J.F. Janak and A.R. Williams, Calculated Electronic Properties of Metals (Pergamon, New York, 1978).
[5] J.P. Pendry, Surf. Sci. 57 (1976) 679.
[6] P.J. Durham, J.B. Pendry and C.H. Hodges, Comput. Phys. Commun. 25 (1982) 193.
[7] J.B. Pendry, Low Energy Electron Diffraction (Academic Press, London, 1974).
[8] D.D. Vvedensky, D.K. Saldin and J.B. Pendry, Comput. Phys. Commun. 40 (1986) 421.
[9] P.A.M. Dirac, Proc. Camb. Phil. Soc. 26 (1930) 376.
[10] L. Hedin and S. Lundqvist, Solid State Phys. 23 (1969) 1.
[11] U. von Barth and L. Hedin, J. Phys. C 5 (1972) 1629.
[12] S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (1980) 1200.
[13] J.P. Perdew and A. Zunger, Phys. Rev. 140 (1965) A1133.
[14] J.C. Slater, The Calculation of Molecular Orbitals, Vol. 5 (McGraw-Hill, New York, 1979).
[15] C.R. Natoli, EXAFS and Near Edge Structure III, Springer Proc. Phys. 2 (Springer, Berlin, 1984) p. 40.
[16] V.L. Shneerson, W.T. Tysoe and D.K. Saldin, Phys. Rev. B 51 (1995) 13015.
[17] J. Stöhr, NEXAFS Spectroscopy, Springer Series in Surface Sciences 25 (Springer, Berlin, 1991) p. 236.