Partial localization of core holes in nonsymmetrical systems

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A phenomenon of partial localization of core holes has been discovered. Fourth-order Green’s function and large-scale configuration interaction calculations have been carried out on the N 1s x-ray photoelectron spectrum (XPS) of a linear NiN₂ cluster. The N 1s core holes in the ionized states of the cluster are to varying extent delocalized between the two geometrically inequivalent nitrogen atoms. In some of the states the core holes are significantly delocalized. Good agreement with the experimental spectra of the N₂/Ni(100)c(2 × 2) chemisorption system is obtained, which makes clear that the effect is to be expected also in this solid-state system. The partial localization of core holes leads to distinct interference effects in the angularly resolved XPS. This can be used for the experimental detection of the effect. The effect is more pronounced for NiP₂, which is also studied here. [S0163-1829(98)05126-1]

I. INTRODUCTION

Core-level spectroscopies represent a very powerful branch of methods for investigating the electronic structure of matter, be it gas phase molecules, liquid, or solid. Being atom-specific in character, core-level spectroscopies provide information on the chemical state of selected atomic species in compounds. The atomic selectivity inherent in these methods is due to the localization of the core holes in ionized or excited states.

The basic property of atomic core levels that favors the localization is that the core levels are spatially very compact and, therefore, the wave functions of the core levels of neighboring atoms do not strongly overlap at reasonable interatomic distances. Thus, the core levels do not strongly interact with each other.

One of the examples illustrating the (dynamical) localization of core holes is the CO₂ molecule. At the symmetrical $D_{\infty h}$ geometry, the O 1s core orbitals are completely delocalized between the oxygen sites due to the high symmetry. However, the direct interaction between the O 1s core levels is very weak as manifested by the splitting between the O 1s orbital energies in the molecule that is only 0.001 eV, and even a slight distortion producing an inequivalence of the O atoms leads to the localization of the core holes in CO₂. Dynamically, vibronic coupling between the two nearly degenerate delocalized $1\sigma_g$ and $1\sigma_u$ levels at $D_{\infty h}$ symmetry gives rise to a strong excitation of the nontotally symmetric vibrational mode and to symmetry breaking upon ionization of the O 1s electrons.¹

The concept that any inequivalence immediately results in localized core holes is commonly accepted in the core-level spectroscopy community. Surprisingly, this concept has never been verified, either theoretically or experimentally. In our view the problem of the core-hole localization is in fact nontrivial. First, it is not evident a priori that the interaction between core levels is always weak enough to result in localized core holes. Second, core holes can also interact with each other through many-electron excitations accompanying their creation. By this means an analysis of the core-hole localization must include, among other aspects, many-body aspects.

A linear NiN₂ cluster is examined here for the localization of the core holes in the N 1s-ionized states. The choice of this molecular object for studying the localization problem is motivated by the following. First, despite the inequivalence of the nitrogen atoms in NiN₂, the N 1s orbitals of the $1\Sigma^+_u$ ground state (GS) of the cluster are markedly delocalized, keeping to a large extent the symmetry properties of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals of the N₂ molecule.² Thus, at the frozen-orbital level (Koopmans’ theorem) the nitrogen core-hole states are largely delocalized. Second, the interaction between the N 1s orbitals in the cluster is not negligible (the splitting between the N 1s molecular orbitals is $\sim 0.1$ eV). Furthermore, very strong many-body effects accompany the ionization of the N 1s electrons of the NiN₂ cluster.²–⁷ The NiN₂ cluster is seen to incorporate all the properties relevant to the problem of localization and, what is important, this cluster is small enough to allow for ab initio many-body treatments. NiN₂ is not only interesting by itself, it also may serve as a good model of the Ni/Ni solid-state system.²–⁷ The computed bonding properties⁵ and the N 1s x-ray photoelectron spectrum²,⁶,⁸ (XPS) are in good agreement with the respective experimental data for the N₂/Ni(100)c(2 × 2) chemisorption system. This allows us to generalize the physics of the core-level ionization obtained for the cluster also to the real solid-state system.

The N₂/Ni(100)c(2 × 2) system is related to the case of weak chemisorption. The N₂ molecules are adsorbed vertically on Ni(100) and are very weakly bound to the surface. The experimental N 1s XPS of this system consists of two intense lines split by $\sim 1.3$ eV and a broad intense structure usually referred to as the “giant satellite” at $\sim 6$ eV above these lines.⁵ The origin of these spectral features has been the subject of numerous and controversial discussions for more than 20 years (see Ref. 10 and references therein). By means
of angle-resolved spectroscopy, the splitting between the two lowest-energy lines has been attributed to the ionization of the two inequivalent nitrogen atoms.\textsuperscript{9,11} The authors of these experimental works based their ideas on the concept of completely localized core holes and used the fact that the electron wave emitted by an atom is focused in the forward direction due to the presence of an atom in front of the emitting one.\textsuperscript{12} The concept of completely localized core holes and the forward peaking of the ionization amplitude have also been used to separate the N 1$s$ XPS of the inequivalent nitrogens.\textsuperscript{9}

In previous theoretical works\textsuperscript{3−7} it has also been \textit{a priori} assumed that core holes created upon ionization of inequivalent atoms must be completely localized. As a result, the ionization of the inequivalent nitrogen atoms was considered as two independent processes localized on the respective atoms. We will show that core holes of inequivalent atoms are not necessarily localized. The discussion of this phenomenon, the partial localization of core holes, is the central subject of the present paper.

II. THEORETICAL APPROACHES AND METHODS

A. Calculations of core-hole states

The ionization potentials and intensities of spectral lines have been calculated by means of the algebraic diagrammatic construction scheme for the one-particle Green’s function consistent through fourth order in the Coulomb interaction [GF ADC(4)].\textsuperscript{13,34} In addition to the above (GF) calculations, multireference direct configuration interaction (CI) calculations were performed using the \textsc{UK GAMESS} package.\textsuperscript{15} The orbital basis of the neutral $^1\Sigma^+$ closed shell GS of the NiN$_2$ cluster was used for the calculations.

Our present approach conceptually differs from all the previous treatments of the problem in that, by using the ground-state orbital basis, we consider simultaneously the ionization of both inequivalent nitrogen atoms, whereas previously the core ionization was treated as two uncoupled processes localized on each of the two inequivalent atoms.

For details we refer the reader to Ref. 2.

B. Exact effective Hamiltonian method

The electronic structure calculations are usually performed in some finite set of basis states. In the case of \textit{ab initio} self-consistent field (SCF) methods, the basis states are atomic orbitals and the secular matrix $H$ constructed in this basis is the Fock matrix. Basis sets for many-body calculations are usually constructed of various excited configurations of SCF determinant wave functions. To take proper account of electron correlation, generally one should use a very large configuration space. In our case the CI and GF secular matrices were $(2\ 500\ 000 \times 2\ 500\ 000)$ and $(114\ 414 \times 114\ 414)$ ones, respectively. The eigenvectors of such large matrices often have a quite complicated structure where many excited configurations are admixed with comparable weights.

To analyze the localization phenomenon quantitatively it is worthwhile to replace the interaction of numerous configurations admixed to the final ionic states by the effective interaction of only a few (in our case two) configurations with the core holes localized on the inequivalent atoms. We used the technique of block diagonalization of Hermitian matrices\textsuperscript{16} for this purpose. With this method one can project the large configuration space of a secular problem onto a small subspace of ‘‘effective’’ or ‘‘dressed’’ configurations of interest, obtaining a small matrix describing the energies of the configurations and the effective interaction among them.

Block diagonalizing the secular matrix $H$ one obtains $H$. Each element block $H_{nn}$ of the block-diagonal matrix $H$ is in fact a uniquely defined exact effective Hamiltonian (EEH) that describes the coupling among the selected basis configurations ‘‘dressed’’ by the interaction with all the remaining configurations.\textsuperscript{2}

To be more specific let us consider the particular case of the N 1$s$ ionized states of the NiN$_2$ cluster. Although we carry out our \textit{ab initio} GF and CI calculations using the GS orbitals of NiN$_2$ as input data, it is convenient to transform all quantities to a representation where the N 1$s$ orbitals are localized on the inequivalent nitrogen atoms. This localized representation we shall use throughout. A most natural choice of the small subspace for the EEH study of the core-hole localization in NiN$_2$ is the subspace of the two N 1$s$ single-hole configurations with the core holes localized on the inner ($c=$ in) and outer ($c=$ out) nitrogens, respectively. This choice has the following advantages. First, the coefficients of the single-hole configurations in the expansion of an eigenvector enter the expression for the intensity of spectral lines (see next section).\textsuperscript{17} Second, the use of the single-hole configurations as the basis for the projection procedure allows us to make the direct comparison between the many-body and one-particle cases. Indeed, one can also project the secular matrix of the SCF method (Fock matrix in our case) onto the space of the two N 1$s$ localized orbitals obtaining the EEH for the ‘‘dressed’’ core-hole states at the one-particle level. Comparing the EEH for the one-particle case with the EEH for the many-body case one can see how the many-body effects influence the energies of the dressed core-hole configurations and the interaction between them.

There is a useful quantity,

$$A_{nn} = (S_{nn} S_{nn}^\dagger)^{1/2},$$

that defines the amplitudes of the dressed interacting configurations of the chosen block $H_{nn}$ of the block diagonal matrix $H$. Here the $S_{nn}$ is the respective block of the block-diagonal part of the matrix $S$ of eigenvectors of $H$ (see Ref. 2). The amplitudes (1) show the contributions of the chosen dressed configurations to the corresponding eigenstates of the original secular matrix $H$. The exact components of the eigenstates of $H$ compiled in $S_{nn}$ and the matrix of eigenvectors $F_{nn}$ of the effective Hamiltonian $H_{nn}$ are related by the matrix of amplitudes $A_{nn}$ (see Ref. 2)

$$S_{nn} = A_{nn} F_{nn}^\dagger.$$

C. Angular distribution of the intensity in the spectra

As already mentioned in the Introduction, the N 1$s$ orbitals of NiN$_2$ are not localized each on its respective atomic site. Consequently, although electronic relaxation drives towards localization, one cannot \textit{a priori} expect that the final ionic states exhibit fully localized core holes. When calculating the intensities one has, therefore, to take into account
possible interference effects arising due to this delocalization of the core hole. In the localized representation the intensity of the \( n \)th ionic state in the XPS reads\(^{18} \)

\[
I_n = \sum_c \tau_c x_c^{(n)}|^2, \quad c = \text{in, out},
\]

where \( \tau_c \) denote the photoionization amplitudes of the N 1s core levels of the inner (\( c = \text{in} \)) and outer (\( c = \text{out} \)) nitrogen atoms in the cluster and \( x_c^{(n)} = (\Psi_n^{N-1}|\hat{a}_c|\Psi_0^N) \) are the spectroscopic amplitudes of the single-hole \( N \), 1s \(-1\) states; \( \Psi_n^N \) and \( \Psi_n^{N-1} \) denote the GS of the \( N \) electron system and the \( n \)th state of the ionized \( N-1 \) electron system, respectively, and the \( \hat{a}_c \) is the annihilation operator for the core electron in the \( c \)th one-electron orbital.

There is another feature of the system that adds complexity to the intensity calculation. The amplitude of the electron wave emitted by the inner atom is strongly peaked in the forward direction due to the scattering by the outer atom.\(^{12} \) The primary electron wave emitted by an atom can interfere with the wave scattered by neighboring atoms leading to a specific angular dependence of the intensity in the XPS. The calculation of the spectral intensity in our case should thus be augmented by the scattering of the outgoing electron by the potential of the final ion, i.e., this scattering should be reflected by the angular dependence of the \( \tau_c \) in Eq. (3).

We introduce a simple model incorporating the scattering of the emitted electron by the neighboring atom. In the dipole approximation the photoionization amplitudes are given by \( \tau_c = A(\mathbf{k} | \mathbf{r} | c) \), where \( | c \rangle \) is the core orbital to be ionized, \( | \mathbf{k} \rangle \) is the wave function of the photoelectron, and \( A \) is the polarization of the ionizing photon. We now assume that \( | \mathbf{k} \rangle \) is essentially a plane wave and that the core orbital ionization cross sections of the two inequivalent nitrogen atoms are equal if the above-mentioned scattering by the other atom is neglected. Then, putting \( \tau_{\text{in}} = \tau \), one readily finds \( \tau_{\text{out}} = \tau e^{i k R \cos \theta} \), where \( R \) is the internuclear \( N-N \) distance, \( \theta \) the emission angle of the photoelectron, and \( k \) the electron wave number (see Fig. 1). For simplicity, we use the asymptotic wave number \( k = \sqrt{2} \varepsilon \), where \( \varepsilon \) is the kinetic energy of the photoelectron.

To account for the relevant scattering of the emitted electron wave by the neighboring nitrogen atom, we now augment \( | \mathbf{k} \rangle \) by a scattering term for the appropriate scattering geometry depicted in Fig. 1. Taking into account the forward peaking of the scattering amplitude\(^{12} \) we write

\[
\tau_{\text{in}} = \left[ 1 + \alpha (1 - e^{-\gamma \theta}) e^{i k R (1 - \cos \theta)} \right],
\]

\[
\tau_{\text{out}} = \left[ e^{i k R \cos \theta} + \beta (1 + e^{-\gamma (\theta - \pi)}) e^{i k R (1 + \cos \theta)} \right],
\]

where \( \alpha, \beta \), and \( \gamma \) are parameters. The parameter \( \gamma \) controls the forward peaking of the scattering amplitude and the parameters \( \alpha \) and \( \beta \) the magnitude of the contributions of electron scattering by the other atom to the photoionization amplitudes of the inner and outer atoms, respectively.

**D. Degree of localization**

To analyze the core-hole localization phenomenon it is useful to introduce a measure of the localization, i.e., a quantity that characterizes to what extent a given core-hole state is localized on the respective atomic site. For this purpose, we introduce here a global degree of localization for the \( n \)th core-hole state, which is the absolute value of the difference between the average core-hole occupation numbers \( n_c \) of the inner (\( c = \text{in} \)) and outer (\( c = \text{out} \)) nitrogen atoms:

\[
D_l(n) = \left| \frac{\langle n_{\text{in}} \rangle_n - \langle n_{\text{out}} \rangle_n}{\langle n_{\text{in}} \rangle_n + \langle n_{\text{out}} \rangle_n} \right|.
\]

The generalization of this definition to other systems is evident. The degree of localization measures the extent (between 0 and 1) to which the state should be viewed as having the electron vacancy localized at one of the atoms. Obviously, in the localized picture, the average occupation numbers \( \langle n_{\text{in}} \rangle_n \) and \( \langle n_{\text{out}} \rangle_n \) are just the sum of squares of all the respective components of the \( n \)th eigenvector. The global degree of localization \( D_l(n) \) [Eq. (5)] rather characterizes the overall vacancy distribution in the \( n \)th core-hole state over the two nitrogen atoms.

It is difficult if at all possible to find a direct connection of the global degree of localization to experimentally observable quantities. To bridge the theory and the spectral experiments it is worthwhile to introduce a projection of the global degree of localization onto the single-hole basis configurations. We define a spectroscopic degree of localization given by

\[
\delta_l(n) = \frac{|x_{\text{in}}^{(n)}|^2 - |x_{\text{out}}^{(n)}|^2}{|x_{\text{in}}^{(n)}|^2 + |x_{\text{out}}^{(n)}|^2},
\]

where \( x_{\text{in}}^{(n)} \) and \( x_{\text{out}}^{(n)} \) are the spectroscopic amplitudes defined in Sec. II C. The spectroscopic amplitudes enter the expression for the intensity (3) and, therefore, can be related to the experimentally measured quantities. It is apparent that the value of the...
TABLE I. Energies, spectroscopic degrees of localization \( d_i^{(n)} \), and spectroscopic amplitudes \( x_i^{(n)} \) of the \( N_1 \) 1s ionized states of the NiN\(_2\) cluster. A localized representation is used; \( c \) refers to the inner and outer nitrogen atoms. Shown are GF ADC(4) results in comparison to the experimental for the N\(_2\)/Ni(100)c(2\(\times\)2) system. All energies in eV.

<table>
<thead>
<tr>
<th>XPS band</th>
<th>( \Delta I_n )</th>
<th>( I_n )</th>
<th>( \Delta I_n )</th>
<th>( x_i^{(n)} ) ( x_i^{(n)} )</th>
<th>( x_i^{(n)} ) ( x_i^{(n)} )</th>
<th>( d_i^{(n)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 main line</td>
<td>0.0</td>
<td>409.00</td>
<td>0.0</td>
<td>-0.013</td>
<td>0.089</td>
<td>( \pi \rightarrow \pi^* + N_1 s^{-1} (\sigma \rightarrow \sigma^*) )</td>
</tr>
<tr>
<td>2 main line</td>
<td>1.3</td>
<td>410.47</td>
<td>1.47</td>
<td>0.456</td>
<td>0.014</td>
<td>( \pi \rightarrow \pi^* + N_1 s^{-1} (\sigma \rightarrow \sigma^*) )</td>
</tr>
<tr>
<td>1 satellite, weak</td>
<td>2.1</td>
<td>411.93</td>
<td>2.93</td>
<td>-0.0018</td>
<td>0.103</td>
<td>( \pi \rightarrow \pi^* )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>412.16</td>
<td>3.16</td>
<td>0.130</td>
<td>0.011</td>
<td>( \pi \rightarrow \pi^* )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>413.10</td>
<td>4.10</td>
<td>0.004</td>
<td>-0.006</td>
<td>( \sigma \rightarrow \sigma^* )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>413.83</td>
<td>4.83</td>
<td>0.027</td>
<td>0.0</td>
<td>( \sigma \rightarrow \sigma^* )</td>
</tr>
<tr>
<td>2 satellite, strong</td>
<td>5.8</td>
<td>415.48</td>
<td>6.48</td>
<td>-0.628</td>
<td>0.051</td>
<td>N ( 1 s^{-1} + \pi \rightarrow \pi^* (\sigma \rightarrow \sigma^*) )</td>
</tr>
<tr>
<td>3 satellite, strong</td>
<td>6.6</td>
<td>415.90</td>
<td>6.90</td>
<td>-0.048</td>
<td>-0.602</td>
<td>N ( 1 s^{-1} + \sigma \rightarrow \sigma^* (\pi \rightarrow \pi^<em>, N_2 \pi \rightarrow \pi^</em>) )</td>
</tr>
<tr>
<td>4 satellite, weak</td>
<td>8.5</td>
<td>417.01</td>
<td>8.01</td>
<td>0.117</td>
<td>0.086</td>
<td>( \sigma \rightarrow \sigma^* (\pi \rightarrow \pi^*) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>417.09</td>
<td>8.09</td>
<td>-0.057</td>
<td>-0.134</td>
<td>( \sigma \rightarrow \sigma^* (\pi \rightarrow \pi^*) )</td>
</tr>
</tbody>
</table>

*The contributions in parentheses denote small admixtures to the ionic states in the order of decreasing importance.

global degree of localization \( D_i^{(n)} \) for a given core-hole state can be different from that of the spectroscopic degree of localization \( d_i^{(n)} \).

When a GF calculation is performed, the \( x_i^{(n)} \) are just elements of the \( n \)th eigenvector of the GF matrix and are thus directly available. Obviously, the \( x_i^{(n)} \) can also be computed by CI calculations, but their computation is more tedious due to GS correlation contained in the spectroscopic amplitudes. Neglecting the influence of GS correlation on the \( x_i^{(n)} \), these amplitudes become directly available also in a CI treatment: they coincide with the respective coefficients of the single-hole basis configurations in the expansion of the CI eigenvector.

**III. RESULTS**

**A. Partial localization**

The results of the GF ADC(4) calculations on the N 1s XPS of the NiN\(_2\) cluster are presented in Table I together with the experimental data of N\(_2\)/Ni(100)c(2\(\times\)2). As seen from the spectroscopic amplitudes and spectroscopic degrees of localization in Table I the core-hole states of the NiN\(_2\) cluster are to a varying extent delocalized over the two nitrogen atomic sites. Some of the states, for example, the pair of satellites at 417.01 eV and 417.09 eV are very well delocalized. Because of this partial delocalization it is not possible to cleanly separate the spectra of the inner and outer nitrogens in the computed spectrum and hence, for the comparison with the experimental spectrum, we combined in Table I the experimental energy positions of the lines in the “inner nitrogen spectrum” and “outer nitrogen spectrum” to get the whole N 1s XPS of the N\(_2\)/Ni(100)c(2\(\times\)2) system. Correspondingly, we list in Table I the spectroscopic amplitudes and not the intensities, since the interference due to the partial delocalization can be accounted for only approximately within our approach (see Sec. II C).

The lowest energy state (GS of the ion) is mostly localized on the outer nitrogen atom and is separated by 1.47 eV from the next state that is mainly localized on the inner nitrogen, in accord with the previous theoretical treatments and the experimental assignment.\(^{9,11}\) According to our calculation, these two states are \( \pi \rightarrow \pi^* \) shake-down satellites (for a detailed analysis of core-hole screening in NiN\(_2\), see Ref. 2). It is significant that, despite the rather large splitting of 1.47 eV, the lowest two states are not completely localized on the inequivalent atoms. The experimental splitting is 1.3 eV.\(^9\) The next two states are more delocalized and also are \( \sigma \rightarrow \sigma^* \) shake-down satellites. They are followed by two \( \sigma \rightarrow \sigma^* \) shake-down satellites at 413.10 eV and 413.83 eV that have very small intensities and cannot be detected experimentally. The degree of localization of these two states is quite different. The satellite at 413.83 eV is almost localized on the inner nitrogen, whereas the state at 413.10 eV is well delocalized. The main lines of the spectrum correspond to the states computed at 415.48 eV and 415.90 eV. They are responsible for the intense and broad band of the experimental spectrum known as “giant satellite.” The two nearly degenerate \( \sigma \rightarrow \sigma^* \) satellite states at 417.01 eV and 417.09 eV we attribute to the experimental feature observed in the spectrum at 8.5 eV. These two states are very well delocalized over the two nitrogen sites. The core-hole states in the energy region from 418 eV to 422 eV in the computed spectrum also exhibit various degree of localization. This part of the computed spectrum is not included in Table I, but can be found in Ref. 2. Some of the states are very well localized (for example, the states at 418.78 eV and 420.71 eV), some of them are very well delocalized (the satellites at 419.66 eV, 420.28 eV, and 422.13 eV).

Thus, the inequivalence of the nitrogen atoms in the NiN\(_2\) cluster does not result in completely localized N 1s core-hole states. Moreover, the localization is state dependent. This aspect of the core-level ionization has not been considered before. Generally, core holes of systems with inequivalent atoms are considered localized on the respective sites.

It is illuminating to analyze the localization phenomenon within the framework of a simple two-level model. Let us
introduce an effective Hamiltonian matrix that describes the interaction of basis states localized on different atomic sites:

$$\mathbf{H} = \begin{pmatrix} \epsilon_1 & U \\ U & \epsilon_2 \end{pmatrix},$$

where $\epsilon_1$ and $\epsilon_2$ are the energies of the basis states and $U$ is the matrix element of the interaction between them. It is useful to introduce the following quantities. The first quantity, the degree of localization, is given by

$$d_i = \frac{C_i^2 - C_j^2}{C_i^2 + C_j^2} = \frac{D}{\sqrt{\Delta^2 + 4U^2}},$$

where $\Delta = \epsilon_2 - \epsilon_1$ and $C_1$, $C_2$ are the components of the localized basis states in the eigenvector (|$C_1$|, |$C_2$|). The degree of localization in this simple case is the difference between the probabilities for the eigenvectors of the Hamiltonian (7) to be localized on the different atomic sites. In this (2 x 2) case the global degree of localization $D^{(2)}$ [Eq. (5)] and the spectroscopic degree of localization $d^{(2)}$ [Eq. (6)] are equal to one another. Furthermore, the degree of localization is identical for both eigenvectors of the Hamiltonian $\mathbf{H}$ in Eq. (7). The second quantity is a mixing angle,

$$\Theta = \arctan \frac{2U}{\Delta + \sqrt{\Delta^2 + 4U^2}},$$

representing the angle of the rotation in the space of the basis states that diagonalizes the Hamiltonian matrix. Thus at $\Theta = \pi/4$ the eigenstates of the Hamiltonian are completely delocalized, while at $\Theta = 0$ the states are exactly localized on different atomic sites. It is easily seen from Eqs. (8) and (9) that the range of the energy splitting $\Delta$ between the basis states, where the eigenstates of the Hamiltonian (7) are still considerably delocalized, is dictated by the interaction matrix element $U$. There are two limiting cases: (i) $\Delta = 0$. In this case the degree of localization is exactly equal to 0 (completely delocalized states) and the mixing angle $\Theta$ is equal to $\pi/4$. (ii) The interaction matrix element is equal to 0. In this case $d_i = 1$ and $\Theta = 0$ (completely localized states).

FIG. 2. The degree of localization $d_i$ as a function of the linear nonsymmetric displacement $\Delta R$ of the O 1s unit in the CO$_2$ molecule and as a function of the Ni-N$_2$ distance $\Delta R$ relative to the equilibrium position of the N$_2$ unit in the NiN$_2$ cluster. To get continuous curves we neglected here the restriction |$C_1$| > |$C_2$| (see Sec. III A). Note the different scaling of the $\Delta R$ axis before and after the breaking point. The inset shows the energy splitting $\Delta$ between the dressed O 1s localized orbitals in the CO$_2$ molecule and that between the dressed N 1s localized orbitals in the NiN$_2$ cluster as a function of $\Delta R$.

Unless dictated by symmetry, we can generally expect $U \neq 0$ and the localization is only partial and depends on the interplay between the splitting $\Delta$ and interaction $U$.

Let us start our treatment of the partial localization phenomenon from the one-particle level of theory. The degree of localization for the O 1s and N 1s orbitals of CO$_2$ and NiN$_2$, respectively, is shown in Fig. 2 as a function of the $\Delta R$, where the $\Delta R$ is the linear asymmetric displacement of the O$_2$ unit in the CO$_2$ molecule and the displacement of the N$_2$ unit relative to the equilibrium Ni-N$_2$ distance in the NiN$_2$ cluster. One can see a very abrupt response in the case of CO$_2$ illustrating the immediate localization of the O 1s orbitals when the symmetrical geometry is slightly distorted. The case of NiN$_2$ is very different from CO$_2$. Despite the nonsymmetrical geometry with respect to the nitrogen atoms, the N 1s orbitals are almost completely delocalized at the equilibrium geometry (the degree of localization is 0.03 and the mixing angle is 45.8°). The region of the Ni-N$_2$ distances at which the N 1s orbitals are still rather delocalized is remarkably wide (approximately from −0.2 a.u. to +0.1 a.u.). This different behavior of the CO$_2$ and NiN$_2$ systems with respect to the localization of the core levels is closely connected to the very different strengths of interaction between atomic core levels in these systems. Interestingly, the degree of localization for NiN$_2$ first increases when pulling the N$_2$ unit away from the Ni atom (Fig. 2). At large Ni-N$_2$ distances ($\Delta R > 1$ a.u.) the degree of localization decreases, asymptotically approaching the expected case of completely delocalized N 1s orbitals of an isolated N$_2$ molecule.

The EEH technique allows us to study the localization phenomenon quantitatively, in terms of the interaction of dressed configurations. In the case of the one-particle level of treatment the (2 x 2) EEH is obtained by the block diagonalization of the (76 x 76) Fock matrix. We are dealing now with dressed atomic core orbitals. The interaction between the N$_{in}$ 1s and N$_{out}$ 1s dressed orbitals of NiN$_2$ is significantly stronger than that of the O 1s dressed orbitals in the CO$_2$ molecule: for NiN$_2$ the matrix element of the interaction is 0.046 eV and for CO$_2$ it is 0.0006 eV. The value of
the interaction matrix element almost does not depend on the displacements of the N$_2$ and O$_2$ units. Contrary to that, the energy splitting between the dressed core orbitals is considerably sensitive to the displacement as demonstrated by the inset in Fig. 2. Thus, we can consider the interaction between the dressed core orbitals as an internal characteristic of the unit under investigation (N$_2$ and O$_2$ in our case), which is not strongly affected by the external perturbation (interaction with the Ni atom for NiN$_2$ and with the C atom for CO$_2$). The energy splitting of the dressed core orbitals in NiN$_2$ changes its sign in the vicinity of the point $\Delta R = 0$. The dressed core orbitals are almost degenerate at this point and the core holes are delocalized. The splitting increases up to $\Delta R \sim 1$ a.u. and then, at large Ni-N$_2$ distances, it gradually decreases approaching the case of an isolated N$_2$ molecule ($\Delta = 0$) where the core holes are again delocalized. Hence, the driving factor for the change from delocalized to localized states and vice versa is the change of the energy splitting between the dressed levels that depends strongly on the strength of the external perturbation. This simple treatment can also be applied to many-electron core-hole states. However, one has to be careful applying this two-level treatment. Indeed, although the core-hole states mostly appear in the spectrum of NiN$_2$ as pairs because of the presence of the two N $1s$ levels, the degree of localization can be very different for two states of a pair (see Table I), indicating that the two-level model (7) cannot be applied straightforwardly in such situations without further information.$^{19}$

For the most intense lines in the spectrum of NiN$_2$ the two-level model applies very well (see Table I). The EEH is obtained by the block diagonalization of the (114 414$^\times$ 114 414) GF ADC matrix. Constructing EEH’s for the core-hole states corresponding to the most intense lines in the N $1s$ XPS of the NiN$_2$ cluster (the pair of states at 409.00 and 410.47 eV and the pair at 415.48 and 415.90 eV) one can see that the matrix elements of the interaction between the dressed N$_{in\,1\,s^-1}$ and N$_{out\,1\,s^-1}$ configurations for these two pairs of states (0.043 eV and 0.034 eV, respectively) are surprisingly close to those obtained by the EEH method at the one-electron level (0.046 eV). The energy splittings between the dressed N$_{in\,1\,s^-1}$ and N$_{out\,1\,s^-1}$ configurations for the two pairs of states are 1.46 eV and 0.42 eV, respectively. Hence, the reason for the localization of the core holes in ionized states of NiN$_2$ is of pure many-body origin: the interaction of the N$_{in\,1\,s^-1}$ single-hole configuration with higher excited ones differs considerably from that of the N$_{out\,1\,s^-1}$ configuration, resulting in the larger energy splitting compared to the one-particle case. However, it should be emphasized that, despite the rather large degree of localization, these two pairs are not completely localized. Moreover, one can find many satellite states that are well delocalized (see also Ref. 2).

B. Angular distribution of photoelectrons

The procedure used in Ref. 9 to separate the spectra of the inner and outer nitrogen atoms is essentially based on the assumption that all core ionized states of the N$_2$/Ni system are well localized either on the inner or outer nitrogen. In this case, the angular dependence of the intensities of the lines in the spectrum, which can be associated with one or the other nitrogen atoms, should be similar for all the states. From Table I it is seen that the degree of delocalization is different for different states. Thus, the interference due to the partial localization affects the intensity of the spectral lines to varying degree, depending on the state considered.

The angular dependence of the intensities of some pairs of intense lines in the spectrum, calculated using our simple model [Eqs. (3) and (4)] is shown in Fig. 3. There are no available high-resolution experimental data on the angular dependence of the line intensities in the N $1s$ XPS of the N$_2$/Ni(100) system. The only available angular resolved data are the ratios between the intensities of the lowest energy lines in the C $1s$ and O $1s$ XPS’s of CO/Ni(100)$c(2\times2)$ (solid line) and of the 400.7- and 399.4-eV lines in the N $1s$ XPS of N$_2$/Ni(100)$c(2\times2)$ (dots).$^9$ [the solid line in the inset of Fig. 3(a)] and that between the 400.7- and 399.4-eV lines in the N $1s$ XPS of the N$_2$/Ni(100)$c(2\times2)$ system$^9$ (the dots in the inset). One can see from Fig. 3(a) that the angular dependence of the intensity of the 409.0-eV line in the computed N $1s$ XPS of the NiN$_2$ cluster is almost isotropic, whereas the intensity of the 410.47-eV line has an interference pattern that is very similar to that shown in the inset. In spite of the angular distribution of the intensity of the 409.0-eV line being close to uniform, one can see a slight modulation of the intensity due to the interference caused by the partial localization (when the core hole is exactly localized on the outer nitrogen, the angular dependence of the intensity for this line is uniform within the drawing line width). The angular dependence of the intensities considerably deviates from a uniform distribution for both components of the pair of $\pi\rightarrow\pi^*$ shake-down satellites at 411.93 and 412.16 eV [Fig. 3(b)] as well as for the pair of main lines at 415.48 and

![Fig. 3](image-url)

**FIG. 3.** The angular dependence of the intensities $I_\theta$ of some intense lines in the N $1s$ spectrum of the NiN$_2$ cluster. (a) $I_{410.47}$ and $I_{409.00}$ are the solid and dashed lines, respectively. Shown in the inset is the experimental angular dependence of the intensity ratio of the lowest energy lines in the C $1s$ and O $1s$ XPS’s of CO/Ni(100)$c(2\times2)$ (solid line) and of the 400.7- and 399.4-eV lines in the N $1s$ XPS of N$_2$/Ni(100)$c(2\times2)$ (dots).$^9$ (b) $I_{412.16}$ and $I_{411.91}$ are the solid and dashed lines, respectively; (c) $I_{415.48}$ and $I_{415.90}$ are the solid and dashed lines, respectively; (d) $I_{417.01}$ and $I_{417.09}$ are the solid and dashed lines, respectively. The angular dependence was calculated using the following values of the parameters in the model (4): $\alpha=2.0$, $\beta=1.0$, $\gamma=6.56$, and $\Gamma=2.069$ a.u. The ionization by photons with the energy of 1486 eV (Al $K\alpha$) has been assumed.
TABLE II. Energies, spectroscopic degrees of localization $d_i^{(n)}$, and spectroscopic amplitudes $x_i^{(n)}$ of the P, 2s ionized states of the NiP$_2$ cluster. A localized representation is used; $c$ refers to the inner and outer phosphorus atoms. Shown are GF ADC(4) results. All energies in eV.

<table>
<thead>
<tr>
<th>$I_n$</th>
<th>$\Delta I_n$</th>
<th>$x_i^{(n)}$</th>
<th>$x_o^{(n)}$</th>
<th>State characterization</th>
<th>$d_i^{(n)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.24</td>
<td>0.0</td>
<td>0.171</td>
<td>0.697</td>
<td>P 2s$^{-1}$, $\pi \rightarrow \pi^*$</td>
<td>0.886</td>
</tr>
<tr>
<td>189.71</td>
<td>1.47</td>
<td>0.743</td>
<td>-0.125</td>
<td>P 2s$^{-1}$, $\pi \rightarrow \pi^*$</td>
<td>0.945</td>
</tr>
<tr>
<td>193.18</td>
<td>4.16</td>
<td>0.091</td>
<td>0.048</td>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>0.564</td>
</tr>
<tr>
<td>193.82</td>
<td>5.58</td>
<td>-0.139</td>
<td>0.020</td>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>0.959</td>
</tr>
<tr>
<td>193.97</td>
<td>5.73</td>
<td>0.298</td>
<td>0.135</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>0.659</td>
</tr>
<tr>
<td>194.99</td>
<td>6.75</td>
<td>0.081</td>
<td>-0.356</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>0.901</td>
</tr>
</tbody>
</table>

415.90 eV [Fig. 3(c)]. Particularly pronounced are the interference patterns for the pair of $\sigma \rightarrow \sigma^*$ shake-up satellites at 417.01 and 417.09 eV [Fig. 3(d)]. Here the angular distribution for both lines is very similar. Interference due to partial localization significantly affects the intensities of some lines in the Ni 1s XPS of the Ni$_2$/Ni(100) system and this effect, in principle, can be detected experimentally. Unfortunately, in NiN$_2$ the states affected most strongly by partial localization are the less intense ones. In other systems the situation may be more favorable for observations.

IV. DISCUSSION

It is generally believed that inequivalent atoms possess localized core holes. A skeptical reader may find our finding of partial delocalization in the Ni 1s XPS of NiN$_2$ to be an artifact of our GF calculation. To be more independent of the method of calculation, we performed large-scale CI calculations (about $2.5 \times 10^6$ configurations) on the Ni 1s XPS of the NiN$_2$ cluster (see Sec. II A). Because of serious computational difficulties we restricted ourselves to finding only the two core-hole states lowest in energy. The energy splitting of these states has been found to be 1.1 eV and the degrees of localization of the core holes in these states obtained were 0.976 and 0.997. One can approximately estimate the degree of localization of the core hole for a pair of lines in the experimental spectrum. Assuming the matrix element $U$ of the interaction between the dressed single-hole configurations to be equal to that of the dressed localized core orbitals (see Sec. III A), formula (8) and the inverse problem for the Hamiltonian (7) readily give the following expression for the degree of localization:

$$d_i = \sqrt{1 - 4 \left( \frac{U}{\Delta I} \right)^2},$$

where $\Delta I$ is the energy separation between the two lines in the spectrum. Using the experimental value for the splitting between the first two peaks in the Ni 1s spectrum of Ni$_2$/Ni(100)c(2x2) (1.3 eV, Ref. 9), and $U$ as obtained by the EEH technique from the results of the SCF calculation on the NiN$_2$ cluster (0.046 eV), we get $d_i=0.997$. This value is very close to that calculated by the GF ADC(4) method (Table I).

To a good approximation the effective interaction $U$ in formula (10) can also be obtained from the split of the respective core molecular orbitals $U=(e_1-e_2)/2$.

V. CONCLUSIONS

Our GF ADC(4) calculations on the Ni 1s XPS of the linear NiN$_2$ cluster show that the Ni 1s core holes in the ionized states of this nonsymmetrical cluster are not completely localized on the inequivalent nitrogen atoms as it has been generally believed. The degree of localization is different for different states and the core holes in some satellite states of the cluster are very well delocalized. This partial delocalization, which is of interest by itself, leads to distinct interference effects in the angularly resolved core-hole spectra of the corresponding levels. The degree of localization strongly depends on the strength of the direct interaction between the configurations that have core holes localized on different atomic sites. When the interaction is strong enough, the external perturbation (say the weak interaction of the N$_2$ unit with the metal atom and the core ionization) cannot give rise to a complete localization of core holes.

The EEH technique is a very powerful tool of analysis. With this method one can extract from the results of different calculations (SCF, CI, GF, etc.) the energies and the effective interaction of selected configurations that make possible the analysis of the problem of interest (particularly the problem of core-hole localization) in some simple and transparent terms. The EEH analysis provides also the ability to estimate...
the degree of localization for some ionized states directly from the experimental XPS (Sec. IV).

The GF ADC(4) calculations on the N 1s XPS of the cluster have demonstrated that this small cluster model suffices to reproduce the main features of the experimental N 1s spectrum of the N$_2$/Ni(100) c(2×2) weak chemisorption system. A good agreement between the computed spectrum of the N$_2$/Ni(100) cluster and experimental spectrum is obtained that makes clear that the phenomenon of partial localization of core holes is not only to be expected in a molecule or cluster but also in a real solid-state system.

In principle, the phenomenon of partial localization of core holes can be detected experimentally by an accurate measurement of the angular dependence of the intensities of spectral lines. We surmise that partial localization of core holes can be observed also in some physisorbed systems.

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17In the case of the GF approach the coefficients of the single-hole configurations in the expansion of an eigenvector are the spectroscopic amplitudes $x_i^{(a)}$ (for the definition, see Sec. II C). In the case of the CI treatment these coefficients are just the weights of the single-hole configurations in the expansion of the CI eigenvector.
19Of course, one could also view the Hamiltonian (7) as the (2×2) EEH constructed for a pair of eigenstates of a large secular problem. Then, the degree of localization (8) is directly related to the spectroscopic degrees of localization introduced in Eq. (6). The $C_1$ and $C_2$ appearing in Eq. (8) and $x_{in}^{(a)}$ and $x_{out}^{(a)}$ appearing in Eq. (6) span $F_{nn}$ and $S_{nn}$, respectively. Equation (2) regulates how one set can be converted into the other set.
20The phosphorous 9s, 5p Gaussian basis set has been contracted to 4s, 2p and a polarization d function has been added ($\alpha = 0.34$).