## CALCULATION OF TRANSITION METAL COMPOUNDS USING AN EXTENSION OF THE CNDO FORMALISM VI. Simple interpretation of many-body effects in the valence shell photoionization of adsorbates by the study of CO/Ni and N<sub>2</sub>/Ni model systems

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The appearance of satellite structure in outer and inner valence shell photoemission spectra of transition metal compounds and adsorbate systems is investigated by application of a manybody Green function technique on SCF-MO-CNDO one-particle wave functions. Three model systems, namely Ni-CO, Ni-N<sub>2</sub> (linear and bridged) are studied with respect to the uncoordinated ligands. The numerical results are shown to be interpretable in a simple, transparent scheme, based on one-particle considerations and interacting configurations. From our results, we conclude that the appearance of satellite structure is mainly connected with metal to ligand charge transfer excitations and intra-ligand excitations. Furthermore it is shown that different relaxation behaviour of  $5\sigma$  and  $1\pi$  orbitals in coordinated CO and N<sub>2</sub> has to be expected.

#### 1. Introduction

During recent years the great amount of photoemission studies on transition metal containing systems has been performed mainly to obtain a deeper understanding of the bonding, as well in transition metal complexes as in adsorbate systems. With growing amount of experimental information the question arose, whether a simple one-particle description, based on Koopmans' theorem, is adequate to interpret the photoemission of these systems. Two facts were mainly responsible to question this simple model, which has been so successfully applied to the investigation of bonding capabilities in a great variety of organic compounds: One is the appearance of pronounced satellite structure observed in the valence and in the core regime of transition metal carbonyles [1] and adsorbates [2]. If the one particle picture is valid, such satellite structure should not be found in the photoemission spectrum. Another hint for the inadequacy of the one-particle description came from angular resolved photoelectron spectroscopy, indicating an orbital sequence for adsorbed carbonmonoxide, which is reversed with respect to the free molecule [3]. Theoretical studies on model systems, based on Hartree–Fock calculations [4], have not been able to explain these inversions in the framework of a oneparticle description. In the previous paper of this series [5] we have shown that for a model system like NiCO an interpretation of satellite structure which is based on many-particle calculations [6] leads to strong deviations from the one-particle picture. These deviations are most pronounced in the ligand region of the photoemission spectrum and have no counterpart in the spectrum of free CO. Similar results have been found for compounds like Ni(CO)<sub>4</sub> or Cr(CO)<sub>6</sub>. The observed deviations are mainly caused by the fact that the uppermost occupied orbitals of CO are no longer outer valence orbitals, if CO is coordinated to a transition metal atom. In some cases, many-body effects were found to be so strong that it became doubtful, whether it is possible to establish a direct connection between an orbital diagram and the observed photoemission spectrum. If such a connection does no longer hold, questions like those concerned with an inversion of orbitals cannot be answered in a straight foreward manner.

To further study these problems, we extended our investigations to two geometric configurations of an isoelectronic model system, namely  $Ni-N_2$ :



Certainly, model systems of this type are not suited to provide a full understanding of the bonding capabilities in surface adsorbates. They allow, however, a detailed analysis of the results of the calculations including many-body effects. This analysis leads to an illustrative interpretation of satellite structure in terms of one electron ionizations and intermixing configurations. Besides the general understanding of satellite structure, such an interpretation additionally allows to test phenomenological approaches to the assignment of satellite structure, as for example the one proposed by Plummer and coworkers [1a]. These authors claim that charge transfer excitations, known to be important in the UV spectra of carbonyl compounds, also determine the satellite structure in these species.

The interpretation given in the present paper, also offers the opportunity to compare the results of calculations performed on adsorbate model systems with those obtained from solid state theories. In this connection it is of special interest to compare our results to those of Schönhammer and Gunnarson [7], who applied a Green function formalism to explain the satellite structure, which accompanies core ionizations of adsorbates. Since UPS and XPS are usually discussed separately in the experimental literature, we divide the discussion of our results in a similar manner, although our interpretation scheme is applicable for the whole energy range. In the present paper, we restrict the analyses to the outer and inner valence shell region. The studies on core ionizations will then be published in a subsequent paper [8].

We start with a short outline of the basic theory and the approximations used in our numerical calculations. We then present a brief discussion of the bonding capabilities, which determine the one-particle energies in these systems. In the fourth section, we discuss the results obtained after inclusion of many-body effects and finally, we present the above mentioned interpretation, using the language of a configuration interaction scheme. In this last section, we also analyse the significance of our results with respect to experimental findings.

#### 2. Theoretical remarks and numerical results

To study many-particle effects we make use of the Green function formalism, a method especially successful in the treatment of ionization processes [6,16]. The one-particle wave functions, needed as an input for the Green function calculations are obtained from an extended version of the CNDO formalism, introduced and exhaustively discussed in Part I of this series [9a]. From the standard CNDO/2 method [9b] our extended CNDO version differs mainly in the use of individual Slater exponents for the radial part of the s, p and d functions of the metal atom. Application to a variety of problems in connection with transition metal containing systems [10] has shown this method to be a valuable tool for these types of systems. As the details of the present calculations are identical to those described in ref. [9a] and the parameters used the same as given in ref. [10a], we do not stress this subject furthermore.

Due to the semiempirical nature of CNDO we can not expect absolute numbers for the different ionization processes. Earlier applications of CNDO/2 to Green function calculations on molecules like  $F_2$ ,  $CO_2$  or Cyclopropane [6c] have, however, shown that many-body effects are reproduced quite well with these simplified one-particle wave functions. Applications of our extended CNDO version to model systems like NiCO and to the real complexes Ni(CO)<sub>4</sub> and Cr(CO)<sub>6</sub> [5] confirm these earlier findings, at least for the "main bands". We therefore expect that the CNDO approach can also provide the basic trends in satellite structure if we use the same numerical boundary conditions as in the above mentioned application on many particle effects in coordinated transition metal systems [5].

The application of the Green function method has been reviewed recently by Cederbaum and Domcke [6a]. It is therefore sufficient to give a few basic facts, stressing, however, those steps in the theory which are of special importance for the simple interpretation scheme, developed in the last section of this paper.

Starting from the Hartree-Fock ground state, ionization potentials are obtained as negative roots of (1):

$$\det(\omega - \varepsilon - \Sigma(\omega)) = 0, \qquad (1)$$

where the usual nomenclature has been used. It has been shown, that  $\Sigma(\omega)$  is diagonal to a good approximation. This reduces the problem to the solution of:

$$\omega - \epsilon_k - \Sigma_{kk}(\omega) = 0, \qquad (2)$$

for each  $\epsilon_k$ . The solutions are labelled  $\omega_{kl}$ , where *l* numerates the different solutions obtained for each  $\epsilon_k$ . In this case each ionization peak may be connected with a specific Hartree-Fock orbital. The intensity of the corresponding ionization processes are approximated by the pole strength:

$$P_{kl} = \left(1 - \frac{\partial}{\partial \omega} \Sigma(\omega) |_{\omega \approx \omega_{kl}}\right)^{-1}, \qquad (3)$$

thus neglecting the influence of the different orbital cross sections and their energy dependance. The self-energy part  $\Sigma_{kk}(\omega)$ , described by a simplified Tamm-Dancoff type approximation proposed by Schirmer and Cederbaum [6b], is given in eq. (4). Further neglect of the, usually small, exchange terms in the denominator leads to eq. (5) [6b], which has been used in our previous papers [5]. In the present paper we use both formulae to investigate the influence of exchange terms on the numerical results. Eq. (4) is too sophisticated to interpret the obtained numerical results in the familiar language of electron configurations. Such an interpretation is, however, easily obtained, if

$$\begin{split} \Sigma_{kk}(\omega) &= \sum_{\substack{n_a n_b \overline{n}_j = 1 \\ a < b}} \frac{\frac{1}{2} (V_{kjab} + V_{kjba})^2}{(V_{kjab} - V_{bjbj} - V_{ajaj} + V_{aabb} + \frac{1}{2} V_{aajj} + \frac{1}{2} V_{bbjj}]} \\ &+ \sum_{\substack{n_a n_b \overline{n}_j = 1 \\ a < b}} \frac{\frac{3}{2} (V_{kjab} - V_{kjba})^2}{(V_{kjab} - V_{bjbj} - V_{ajaj} - V_{aabb} + \frac{3}{2} V_{aajj} + \frac{3}{2} V_{bbjj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1 \\ a < b}} \frac{V_{kjaa}^2}{(\omega + \epsilon_j - 2\epsilon_a + [V_{aaaa} - 2V_{ajaj} + V_{aajj}]} \\ &+ \sum_{\overline{n_a \overline{n}_j n_j = 1}} \frac{\frac{1}{\omega + \epsilon_j - 2\epsilon_a + \epsilon_b - [V_{abab} - V_{bjbj} - V_{ajaj} + V_{aabb} + \frac{1}{2} V_{aajj} + \frac{1}{2} V_{bbjj}]} \\ &+ \sum_{\overline{n_a \overline{n}_j n_j = 1}} \frac{\frac{1}{\omega + \epsilon_j - 2\epsilon_a - \epsilon_b - [V_{abab} - V_{bjbj} - V_{ajaj} + V_{aabb} + \frac{1}{2} V_{aajj} + \frac{1}{2} V_{bbjj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j n_j = 1}} \frac{\frac{3}{\omega + \epsilon_j - 2\epsilon_a - \epsilon_b - [V_{abab} - V_{bjbj} - V_{ajaj} - V_{aabb} + \frac{3}{2} V_{aajj} + \frac{3}{2} V_{bbjj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j n_j = 1}} \frac{V_{kjaa}^2}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaaa} - 2V_{ajaj} + V_{aajj}]}, \end{split}$$

$$(4)$$

$$\Sigma_{kk}(\omega) = \sum_{\substack{n_a n_b \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj} + V_{aajj}]}, \qquad (4)$$

$$+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V_{kjab}^2 + V_{kjba}^2 - V_{kjab} V_{kjba})}{(\omega + \epsilon_j - 2\epsilon_a - [V_{aaaa} - 2V_{ajaj}]} \\ &+ \sum_{\substack{n_a \overline{n}_j \overline{n}_j = 1}} \frac{2(V$$

the affinity poles resulting from  $n_j = \overline{n_a} = \overline{n_b} = 1$  are neglected. This approximation is equivalent to a complete neglect of ground state correlation [6b] in the initial *N*-particle system. From numerical tests we conclude, that the inclusion of affinity poles in eq. (4) leads to more accurate values for ionization potentials, not affecting, however, the general spectral habitus. With this justification in mind, the affinity poles may be disregarded for interpretation purposes, leading to a description of the ionization process, where the ground state of the initial system with energy  $E_0^{(N)}$  is represented by a Hartree–Fock determinant, while the ion state is described by the following configuration-interaction ansatz:

$$|\psi_n^{N-1}\rangle = \left(c_0^{(n)}a_k + \sum_{jab} c_{jab}^{(n)}a_j^{\dagger}a_d a_b\right) |\psi_{\rm HF}\rangle.$$
(6)

Considering the ion state, the interaction between the Koopmans state  $a_k |\psi_{HF}\rangle$  and the configuration  $a_j^{\dagger}a_a a_b |\psi_{HF}\rangle$  is mainly given by  $V_{kjab}$  and  $V_{kjba}$ . The latter configuration splits into two doublet and one quartet states. In first order electron interaction, the energy of the two doublet states — the quartet state may be disregarded [6b] — is given by:

$$E_1 = -\epsilon_a - \epsilon_b + \epsilon_j + V_{abab} - V_{bjbj} - V_{ajaj} + V_{aabb} + \frac{1}{2}V_{aajj} + \frac{1}{2}V_{bbjj}, \qquad (7a)$$

$$E_2 = -\epsilon_a - \epsilon_b + \epsilon_j + V_{abab} - V_{bjbj} - V_{ajaj} - V_{aabb} + \frac{3}{2}V_{aajj} + \frac{3}{2}V_{bbjj} , \qquad (7b)$$

where we set  $E_0^{(N)} = 0$ .

Neglecting the exchange terms, the energy difference between  $E_1$  and  $E_2$  vanishes, which is equivalent to the use of formula (5) instead of (4). The resulting energy reads:

$$E_3 = -\epsilon_a - \epsilon_b + \epsilon_j + V_{abab} - V_{bjbj} - V_{ajaj} .$$
(8)

If the energy  $E_3$  is similar to the energy of the Koopmans state, the interaction matrix element determines the resulting effects, which are discussed in the next section. The explicit numerical values for  $E_3$  and the interaction matrix elements with the considered Koopmans state are given in the appendix. The theoretical spectra, shown in figs. 4–10 are obtained as a superposition of ionization peaks resulting from the solution of the Dyson eq. (2) for different k.

The height of the bars corresponds to the calculated pole strength. The final spectra are obtained by folding each peak with a Lorenzian curve of 1 eV/FWHM. The peaks are labelled by the symmetry of the orbitals from which they originate. The usual assignment for CO is used throughout the paper for all occurring ligand states. The metal states are classified with respect to their local symmetry in the molecules as  $\delta_M$ ,  $\pi_M$  and  $\sigma_M$ , and if this differentiation is not necessary as M. As the direct superposition of the solutions of (2) for different k neglects orbital specific cross sections we have plotted the orbital specific spectral densities as an example in the case of NiCO (fig. 8c).

### 3. One-particle considerations

As one of the main purposes of the present investigation is the development of a picture, allowing a simple interpretation of many-body effects, we start the presentation of our results with a qualitative discussion of the bonding capabilities in the studied model systems.

Fig. 1 illustrates the interaction of carbon monoxide and nitrogen with a nickel atom in the linear arrangement. The geometries used in our calculations were evaluated from related complex compounds: For NiCO the bond length was taken from Ni(CO)<sub>4</sub> [11]. For NiN<sub>2</sub> averaged values from several compounds were chosen, e.g. Ni-N = 1.82 Å and N-N = 1.11 Å [11]. In the linear case, the metal ligand  $\sigma$  bond is built by interaction of the 5 $\sigma$  orbital from N<sub>2</sub> with a Ni d/s mixture, resulting in a destabilization of the s and d level of the metal. The  $\pi$ -type interaction leads to a slight destabilization of  $2\pi$  and an increasing separation of the metal d levels. Thus the interaction is quite similar to the case of NiCO [4b,5].

The main difference between nitrogen and carbonmonoxide is the absence of the centre of inversion in CO causing a nonbalanced distribution of coefficients in the MO's, not affecting the phase relations of the AO's.  $5\sigma$  as well as  $2\pi$  exhibit larger coefficients on the electropositive carbon atom, leading to more pronounced  $\sigma$ 



Fig. 1. Qualitative MO scheme of carbon monoxide and nitrogen interacting with a Ni atom in linear geometry.

	к <sub>со</sub>	κ <sub>CO</sub>	κ <sub>NiC</sub>	$\kappa_{\rm NiC}^{\pi}$	$\kappa_{NN}^{\sigma}$	$\kappa_{NN}^{\pi}$	κ <sub>NiN</sub>	$\kappa_{NiN}^{\pi}$	$K_{NiN_2}^{\sigma}$	$\kappa_{NiN_2}^{\pi}$
CO	0.94	1.66								
Ni-CO	0.92	1.38	0.58	0.41						
N <sub>2</sub>					1.0	2.0				
Ni-N <sub>2</sub>					1.0	1.88	0.39	0.13		
N–N Ni					1.0	1.63			0.4	0.4

Wiberg indices of free and coordinated carbon monoxide and nitrogen as calculated by CNDO

Table 1

donor and  $\pi$  acceptor abilities in the case of coordination. This is documented by table 1, collecting the Wiberg indices [12,10b] of the free and coordinated systems. Evidently the larger Wiberg index of the N<sub>2</sub> bond with respect to CO is maintained on coordination, whereas the metal-CO bond index is considerably larger than the metal-N<sub>2</sub> index. These results are in agreement with considerations based on chemical intuition and on experimental findings [11].



Fig. 2. Qualitative MO scheme of nitrogen interacting with a Ni atom in bridged geometry.

Fig. 3. (a)  $\sigma$ -type interaction of nitrogen with a Ni atom in bridged configuration; (b)  $\pi$ -type interaction of nitrogen with a Ni atom in bridged configuration.

Fig. 2 shows the situation for the bridged geometry, where the Ni–N and the N–N distances are the same as in the linear geometry. Here the donating MO of N<sub>2</sub> is that one of the degenerated  $1\pi$  orbitals which is situated in the plane of the molecule. This orbital is slightly stabilized by the interaction, destabilizing the Ni d/s  $\sigma$ -type orbitals. The corresponding  $2\pi$  orbital leads to a similar  $\pi$ -acceptor effect as in the linear case by coupling to the  $\pi$ -type d orbitals in the cluster plane (see fig. 3). According to fig. 3 the Wiberg index of the metal-ligand interaction is split, leading to the conclusion that, caused by the larger  $\pi$ -acceptor ability in the bridged geometry, this bond is rather strong compared to the linear case. The total N–N bond index is smaller in the triangular arrangement, because of the distinct decrease of the  $\pi$  interaction in N<sub>2</sub>. Thus, the N–N bond is obviously stronger affected in a bridged, than in a linear geometry and one may speculate, this configuration to be favoured in dissociative adsorption of N<sub>2</sub>.

From a general point of view, the qualitative discussion illustrates that in the one particle picture of ionization the orbitals of the free molecules may be well identified in the coordinated systems. Whether this strong connection between free and complexed ligands is retained in the many-particle description of ionization or not will be investigated in the next section.

#### 4. Many-body effects in uncoordinated systems

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Since in an earlier paper [5] we have already presented numerical results on free and coordinated carbon monoxide, without detailed assignment of satellite structure, the analysis of CO will be given here in connection with the results on free and complexed nitrogen.

The one-particle and the many-particle corrected ionization spectrum (shortly termed: "many-particle spectrum" in the following) of free CO are reproduced in fig. 4. As an example we have plotted the solution of the Dyson eq. (2) with  $\Sigma(\omega)$  in the form of (5) in fig. 12 of the appendix. Each graph contains the information about the redistribution of the Koopmans state, according to many-particle interactions. The energetic position of a spectral line is given by an intersection point of the straight line with the solid curve, while its intensity is approximated by the value of  $P_{kl}$  (thin line) at the intersection points.

The poles of the self-energy part can be assigned to one-particle-two-hole state configurations. The energies of the different configurations as well as the interaction matrix elements of these configurations with the Koopmans state are given in table 2 of the appendix. If we refer to the so called monopole selection rules, it may be generally stated that the configuration energies of the  $\pi\pi^*$  excitations are always lower than those of the  $\sigma\sigma^*$  excitations. This had to be expected from the UV data of CO [10c, 13].

The  $3\sigma$  orbital is of inner valence shell type, because it is in energetical vicinity to configurations, originating from outer valence shell orbitals. The strongest inter-



Fig. 4. (a) One-particle spectrum of carbon monoxide. (b) Many-particle corrected spectrum of carbon monoxide as obtained by using formula (5).

actions with the Koopmans state are created by  $6\sigma 4\sigma^{-1}5\sigma^{-1}$  and  $2\pi 4\sigma^{-1}1\pi^{-1}$ , which means, that the poles at -37.4 and -44.7 eV must be assigned to mixtures of configurations, leading to a transition with more Koopmans "character", assignable to the peak at higher binding energy. In contrast to the  $3\sigma$  orbital, the other orbitals are of outer valence type. Thus the poles of  $\Sigma$  are always at lower energies.

In the case of the  $4\sigma$  orbital, the most important interactions are  $2\pi 4\sigma^{-1} 1\pi^{-1}$  and  $2\pi 1\pi^{-1}5\sigma^{-1}$ . The admixture of the latter configuration has been interpreted in terms of an intramolecular charge transfer [14], since it may be regarded as a charge transfer between the two free electron pairs at oxygen and carbon of carbon monoxide. From the pole strengths it must be concluded, that the peak at lowest binding energy is mainly the Koopmans state, while the other ones are dominated by the mentioned configurations. The  $1\pi$  orbital mostly interacts with the  $2\pi 1\pi^{-2}$ and the  $6\sigma 1\pi^{-1}5\sigma^{-1}$  configurations, resulting in an only slightly shifted Koopmans state at low binding energy and a satellite at 37.2 eV, corresponding mainly to the admixed configurations. The uppermost orbital 5 $\sigma$  mixes with  $6\sigma 4\sigma^{-1}5\sigma^{-1}$ ,  $2\pi 4\sigma^{-1}1\pi^{-1}$  and  $2\pi 1\pi^{-1}5\sigma^{-1}$ . The second configuration is complementary to the  $2\pi 1\pi^{-1}5\sigma^{-1}$  configuration in the 4 $\sigma$  case and may be as well termed an intramolecular charge transfer with respect to  $5\sigma$ . This configuration leads to the most pronounced satellite at 40.2 eV (accidentally the corresponding intersection point is not included in the graph of fig. 12). The many-particle spectrum (fig. 4b) is a superposition of all the discussed poles, where the one-electron parency is labelled by the corresponding orbital notation. The heights of the lines are proportional to the calculated pole strengths.

In the discussion presented so far, it has been assumed that the doublet states, created by the 1p2h configurations have the same energy. If this restriction is removed, a greater manifold of possible poles appears. As an example, the influence of doublet state splitting is discussed for the 30 orbital. The 30 Koopmans state interacts with mainly two configurations, originating from  $\sigma\sigma^*$  and  $\pi\pi^*$  excitations (in the sense discussed above). Taking into account different energies for the resulting doublet states, the configuration-interaction problem increases from rank  $3 \times 3$ to  $7 \times 7$ . Since the doublet splitting is described by exchange terms, the seven new eigenvalues should lie in the same energy range as the former ones. Obviously, the main pole of  $3\sigma$  is reobtained and the former single  $3\sigma$  satellite is now split up into three main components. Fig. 5a shows the numerical results for all orbitals, where only poles with pole strength greater than 0.01 are included. The figure illustrates that results, similar to those outlined for the  $3\sigma$  orbital, are found for all satellites. A comparison of fig. 5a with the experimental spectrum (fig. 5b) [15] brings about that the general habitus of the calculated spectrum of CO agrees quite satisfactorily with experiment.

To underline the comparability of nitrogen with carbon monoxide, it is necessary to go through the detailed analysis also in the latter case. Fig. 6 collects similar information as fig. 4 on the one-particle and the many-particle spectrum of nitrogen. Table 3 contains the interaction matrix elements for the given configurations. In general, we find that due to the higher symmetry of N<sub>2</sub> the number of interacting configurations decreases. Nevertheless, analogous to carbon monoxide, the  $\pi\pi^*$ excitations are found at lower energies than the  $\sigma\sigma^*$  transitions. The same types of configuration are important as in CO. Especially for  $4\sigma$  and  $5\sigma$  these are the configurations with intramolecular charge transfer character [14]. In the case of the  $1\pi$ 



Fig. 5. (a) Many-particle corrected spectrum of carbon monoxide as obtained by using formula (4). (b) Experimental spectrum of CO from ref. [15].

orbital we find a typical minimal basis and ZDO artefact, leading to vanishing ionization poles of  $\Sigma$ . Therefore in this calculation, no satellite connected with the  $1\pi$ orbital is obtained in the inner valence shell region. Only a slight shift of  $1\pi$  in the outer valence shell region is found. Contrary to this, the  $4\sigma$  and  $5\sigma$  orbitals are shifted by interaction with the intramolecular charge transfer configurations to



Fig. 6. (a) One-particle spectrum for nitrogen. (b) Many-particle corrected spectrum of nitrogen as obtained by formula (5).

lower binding energies, thus explaining the different relaxation behaviour of outer valence  $\pi$  and  $\sigma$  orbitals [16].

If we now include the energy splitting of the doublet states, we have to turn to fig. 7a, where the splitting of satellite lines is again obvious by comparison with fig. 6b. The most pronounced effect is recognized in the  $3\sigma$  main peak, which now



Fig. 7. (a) Many-particle corrected spectrum of nitrogen as obtained by using formula (4). (b) Experimental spectrum of nitrogen from ref. [15].

consists of two intensive components. This is due to the fact that by chance a doublet state, resulting from the  $6\sigma 4\sigma^{-1}5\sigma^{-1}$  configuration is in the energetic vicinity of the expected intersection point of  $(\omega - \epsilon_{3\sigma})$  with  $\Sigma$ . Such effects should occur more frequently, whenever the basis of the SCF calculation becomes larger. Therefore it is not surprising, that in Green function calculations, starting from ab

initio Hartree–Fock results, as for instance those of Schirmer et al. [17], more satellite lines are found. This, however, does not affect the general habitus of the satellite structure. Results from equation-of-motion [18] and traditional configuration-interaction methods [14] are also in quite satisfactory agreement with our findings, especially, if one compares the main admixing configurations. In these calculations it has also been found that the intramolecular charge transfer configurations are the leading factors in determining the occurrence of satellite structure accompanying ionization from  $4\sigma$  and  $5\sigma$ . Additionally, the satellites originating from  $1\pi$  ionizations are found to be very small. This is in good agreement with our results and gives further justification to the use of the CNDO method.

Concluding the discussion of  $N_2$ , a comparison of fig. 7a with the experimental spectrum (fig. 7b) [15,19] shows that, as in the case of CO, the calculated spectrum contains the main features found in the experiment.

#### 5. Many-particle effects in coordinated systems

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As mentioned in the introduction, we restrict ourselves in this paper to the discussion of satellite sturcture, not considering the differences in relaxation shifts of  $5\sigma$  and  $1\pi$  orbitals in NiCO, with which we have dealt in detail in a previous paper [5]. To emphasize, with respect to the occurrence of satellite lines, the close connection between free and coordinated molecules, we start our discussion with some general remarks on the self-energy part, being especially applicable to these systems.

The self-energy part of the coordinated system may be divided into two parts:

$$\Sigma(\omega) = \Sigma^{\widetilde{L}}(\omega) + \Sigma^{\widetilde{LM}}(\omega), \qquad (9)$$
  
where  $\Sigma^{\widetilde{L}}(\omega)$  denotes the part of  $\Sigma(\omega)$ , containing only contributions from the  
ligands, while  $\Sigma^{\widetilde{LM}}(\omega)$  collects all the other contributions. If the ligand is only

$$\Sigma^{\widetilde{L}}(\omega) \approx \Sigma^{L}(\omega) , \qquad (10)$$

where  $\Sigma^{L}(\omega)$  is the self-energy part of the pure ligand.

slightly affected upon coordination, one may assume:

Two cases may be distinguished:

(i) If  $\Sigma_{kk}^{\tilde{L}M}(\omega)$  has no pole in the energetic vicinity of an intersection point of  $(\omega - \epsilon_k)$  with  $\Sigma_{kk}^{L}(\omega)$ , the resulting eigenvalue will be only slightly affected by complexation. In such a case, we may expect a one to one correspondence between main and satellite lines in the free and the coordinated ligand.

(ii) If a pole of  $\Sigma_{kk}^{LM}(\omega)$  has nearly the same energy as the mentioned intersection point, the band intensity connected with the former pole of the Green function in the uncoordinated system is distributed over the resulting new lines of the coordinated system. The energy separation and the relative intensities of these lines depend on the interaction matrix element. Thus one finds more lines in the coordinated, than in the uncoordinated system.

The detailed analysis of the numerical results will give illustrative examples of these types of interaction. We proceed in our further discussion in the orbital specific manner, which we have already used for carbon monoxide and  $N_2$ , and restrict ourselves to a detailed study of the results on NiCO, only discussing the data on NiN<sub>2</sub> in a comparative way.

Fig. 8 shows the one-electron (fig. 8a) and two many-particle spectra (figs. 8b



Fig. 8. (a) One-particle spectrum of linear Ni-CO. (b) Many-particle corrected spectrum of Ni-CO, eq. (5).



Fig. 8. (c) Orbital specific spectral density obtained from eq. (2) with  $\Sigma(\omega)$  in the form of eq. (4). (d) Many-particle corrected spectrum of Ni-CO obtained as superposition of the individual spectra of (c), using eq. (4).

and 8d) of linear NiCO. Additionally we present as an example in fig. 8c the orbital specific spectral density which leads to fig. 8d. The orbitals are labelled using the nomenclature of free CO. The numerical data, leading to fig. 8b, are given in table 4. In spite of the close similarity of the orbitals of free CO with ligand orbitals in NiCO, the many-particle spectra look quite different. A closer check will, however, bring about a rather strong correspondence. For the  $3\sigma$  orbital we find much more intermixing configurations in the coordinated system than in the free molecule. Nevertheless, the discussion can be restricted to only those three relevant configurations, exhibiting a large interaction with the  $3\sigma$  Koopmans state. These are  $2\pi 3\sigma^{-1}\pi_{\rm M}^{-1}$ ,  $6\sigma 4\sigma^{-1}5\sigma^{-1}$ , and  $2\pi 4\sigma^{-1}1\pi^{-1}$ . At this point the similarity to free carbon monoxide becomes obvious in so far, as the latter two configurations are dominant also in CO, while the first one is an additional configuration, which only exists in coordinated systems, since it has metal to ligand charge transfer character. The intermixing leads to three intensive lines, where the one at lowest binding energy involves the smallest charge transfer contribution and may thus be correlated with the  $3\sigma$  satellite at 37.4 eV in free CO (fig. 4). The old Koopmans state in CO strongly interacts with the charge transfer configuration, now leading to two lines. The one at lower binding energy also exhibits some  $2\pi 4\sigma^{-1}1\pi^{-1}$  character. The orbitals  $4\sigma$ ,  $1\pi$  and  $5\sigma$ , which are all outer valence orbitals in the free ligand become inner valence orbitals by bonding to the metal atom. The loosely bound d electrons of the metal atom give rise to a considerable number of poles in the energy range of the above mentioned orbitals. In ref. [5] we have shown that this is not only true for model systems like NiCO, but also for real carbonyl complexes, such as  $Ni(CO)_4$ and  $Cr(CO)_6$ . Besides the poles found in the free ligand, three new poles are obtained from  $4\sigma$  originating from interaction with the configurations  $s_M 5\sigma^{-1} 4\sigma^{-1}$ ,  $2\pi 4\sigma^{-1}\pi_{\rm M}^{-1}$ , and  $2\pi 5\sigma^{-1}\pi_{\rm M}^{-1}$ . These interactions lead to a split of the main peak into the three satellites at low binding energy, followed by the only slightly affected satellites of free CO and an additional satellite caused by the metal levels. The results for  $1\pi$  and  $5\sigma$  are similar to those found for  $4\sigma$ , taking into account the configurations listed in table 4. A different situation is, however, yielded for the ionization from metal orbitals k<sub>M</sub>. All interacting configurations are now of higher energy than the corresponding Koopmans state and carry a hole in just the orbital  $k_{\rm M}$ . The most important of these configurations is  $s_{\rm M} k_{\rm M}^{-1} \sigma_{\rm M}^{-1}$ , leading to strong satellite structure in the energy region of ligand states, assignable to the metal orbital. It is remarkable that the metal p states are of minor importance for the determination of satellite structure. This is due to the diffuse character of these orbitals, yielding small interaction matrix elements. The latter result is in good agreement with our calculation of UV spectra of transition metal carbonyls [10c]. In fig. 8b the satellites belonging to ligand ionization are labelled in the same fashion as the parent orbital in free CO, while the metal satellites are separately assigned. In turning from fig. 8b to fig. 8c, where formula (4) has been applied, obviously only minor alterations occur, so that a detailed discussion is superfluous.

Since NiCO is a model system, we cannot give any comparison of fig. 8c with

experimental data at this point. Nevertheless we think that some general conclusions on the appearance of satellite lines may be drawn. Before we turn to this point, we complete the discussion on model systems and first present our data on the model system  $NiN_2$ .

Fig. 9 contains the one-electron and many-particle spectra of linear  $NiN_2$ . The detailed numerical information on this system is collected in table 5. The basic



Fig. 9. (a) One-particle spectrum of linear Ni $-N_2$ . (b) Many-particle corrected spectrum of linear Ni $-N_2$  as obtained by formula (5).

results are completely analogous to those obtained on NiCO. The changes, introduced in the range of the ligand ionizations upon coordination, are more drastic for N<sub>2</sub> than for CO, being strongest for the orbital  $1\pi$ . While we only find one shifted Koopmans state for  $1\pi$  in free N<sub>2</sub>, we are now confronted with seven satellite lines, originating from the  $1\pi$  orbital in NiN<sub>2</sub>. Similar to NiCO, metal ligand charge transfer configurations become important for all the ligand orbitals in addition to those



Fig. 10. (a) One-particle spectrum of bridged Ni $-N_2$ . (b) Many-particle corrected spectrum of bridged Ni $-N_2$  as obtained by formula (5).

configurations, which dominate in free N<sub>2</sub>. In the case of the metal d orbitals, we also find, in principle, the equivalent situation as in NiCO, but the metal satellites are more pronounced in the NiN<sub>2</sub> case. A different situation with respect to CO is met if we investigate the orbital specific relaxation behaviour. For NiCO we find a stronger  $1\pi$  than  $5\sigma$  relaxation [5], causing a decrease in energy separation between these orbitals relative to free CO. This is not found in NiN<sub>2</sub>. On the contrary, we conclude from our calculation that the ionization from  $5\sigma$  yields a stronger relaxation shift than that from the  $1\pi$  orbital, similar to free N<sub>2</sub>. An interchange of the orbital sequence is therefore not to be expected. As these results are not altered using formula (4), we do not present the corresponding data. Instead, we proceed directly to the bridged model system.

Fig. 10 shows one-electron and many-electron spectra for the triangular case and table 6 summarizes the detailed data. A comparison to the linear case (table 5) shows that although the bonding situation is quite different, the main configurations and their energies are similar, and therefore the many-body effects are nearly the same. This becomes quite evident if one looks at the sequence of marked satellites, which is approximately identical in both cases. One is therefore not surprised that the relaxation behaviour of  $5\sigma$  and  $1\pi$  shows the same trend as for the linear NiN<sub>2</sub> arrangement. From a quantitative point of view one would even predict the  $5\sigma-1\pi$  separation to be larger in bridged than in linear geometry, an effect, which is already indicated in the one-particle spectra. Anyway, the orbital sequence of adsorbed and free N<sub>2</sub> should be the same, not effected by different coordination sites. Application of formula (4) does not lead to different conclusions in this case either.

#### 6. Systematizing conclusions

The results shown in the previous section, clearly demonstrate that the incorporation of many-particle effects in the description of ionizations from coordinated transition metal systems is necessary for even a qualitative understanding of the photoelectron spectra of these systems. Although our numerical results are based on model systems, and obtained from semiempirical MO data, they nevertheless can be used as a basis for a qualitative understanding of many particle effects in coordinated systems.

Let us first consider the region of the ligand states: Two different types of configurations are important for an interaction with the Koopmans state: (a) the configurations, already important in the uncoordinated ligand; (b) configurations including occupied metal orbitals, especially  $2\pi L^{-1} \pi_{\rm M}^{-1}$  and  $2\pi \pi_{\rm M}^{-2}$ , where L denotes a ligand orbital.

In group (a) the main contributions come from intramolecular charge transfer configurations and are of special interest with respect to  $4\sigma$  and  $5\sigma$  orbitals. The group (b) configurations, which are the most important factors in determining the

breakdown of the one-particle picture, are mostly charge transfer configurations, where an electron transfer occurs from the metal to the ligand. By coupling to these configurations, the positive charge is delocalized over the whole molecule. Out of the charge transfer configurations, the main coupling to the Koopmans state  $L^{-1}$  is given by:  $2\pi L^{-1}\pi_{M}^{-1}$ .

Two reasons may be responsible for this behaviour: (i) The interaction matrix element, approximated by  $V_{L2\pi L\pi M}$ , is fairly large. (ii) The Koopmans state and the mentioned configuration have similar energy.

The validity of the last statement can be rationalized as follows: The UV excitation  $\pi_{\rm M} \rightarrow 2\pi$  in neutral NiCO is given by:

$$E_{\pi_{M} \rightarrow 2\pi} = \epsilon_{2\pi} - \epsilon_{\pi_{M}} - V_{\pi_{M} 2\pi \pi_{M} 2\pi}$$
  
= 4.6 - (-9.4) + (-8.2)[eV] = 5.8 eV

The energy of the corresponding excitation in the ion, with a hole in L reads:

$$E(L)^{\pi_{M} \to 2\pi} = -\epsilon_{L} + (\epsilon_{2\pi} - \epsilon_{\pi_{M}} - V_{\pi_{M} 2\pi \pi_{M} 2\pi}) + (V_{L\pi_{M} L\pi_{M}} - V_{L2\pi L2\pi}) + (V_{L\pi_{M} L\pi_{M}} - V_{L2\pi}) + (V_{L\pi_{M} L\pi_{M}} - V_{L\pi}) + (V_{L\pi_{M} L\pi_{M}} - V_{L\pi}) + (V_{L\pi_{M} L\pi_{M}} - V_{L\pi}) + (V_$$

This may be interpreted as Koopmans ionization out of L superimposed by a  $\pi_M \rightarrow 2\pi$  UV excitation (see above) and an additional correction term, which is characteristic for the created hole L. While all  $V_{L2\pi L2\pi}$  in NiCO are of the same order of magnitude, e.g. 13.5 eV, the electron integrals including metal orbitals, are only about half that value. This leads approximately to the following result:

## $E(L)^{\pi_M \to 2\pi} \simeq -\epsilon_L$ .

If in addition to the validity of condition (b), condition (a) is fulfilled, too, we expect a strong interaction of the Koopmans state with the quoted configuration. This leads to a situation in the most simple case, depicted in fig. 11, where we find two new lines with energy  $E_a$  and  $E_b$ . Considering the numerical results in detail (see appendix), we find, that in most cases  $E(L)^{\pi_M \rightarrow 2\pi}$  is smaller than the negative orbital energy,  $-\epsilon_L$ , resulting in a negative energy for the  $\pi_M \rightarrow 2\pi$  excitation energy in the presence of a hole in orbital L [20]. These findings exhibit strong analogies to a theory of core ionization, developed by Schönhammer and Gunnarson [7]. Using their language, this is equivalent to a stabilization of an unoccupied ligand orbital below the Fermi level, due to the presence of a hole. This will be further discussed in connection with core hole ionization in a subsequent paper [8].

All discussions given above were concerned with ligand states, so that the metal states remain to be discussed. For the metal states themselves only configurations with one hole in the metal orbital under consideration are of importance. The most important of all these is  $sM^{-1}\sigma_{M}^{-1}$ , with M being the discussed metal level. The energy of this and all other mentioned configurations is considerably higher than the Koopmans energy  $-\epsilon_{M}$ , so that the strong effects, observed for the ligand states,



Fig. 11. Qualitative interaction diagram of a Koopmans state with an intermixing configuration.

do not appear in these cases. Nevertheless, the weak coupling to configurations induce some satellite structure at the higher binding energy side of the Koopmans peak. These metal satellites are predicted to be separated by about 6-8 eV from the main metal peaks.

Experimental evidence for additional satellite structure at the high binding energy side of metal band emission has been found on clean Ni surfaces and has been theoretically interpreted by Penn as coupling of excitons to the metal states [21]. This interpretation is completely equivalent to our findings. To our knowledge, corresponding satellite structure has not been clearly identified for adsorbate systems, whereas hints are given [2d] to such structure at the high binding energy side of the ligand emissions in these systems. In real carbonyl compounds, however, the occurrence of ligand satellites is a well established experimental fact. This has been mainly shown by Plummer and coworkers [1a] for a variety of transition metal carbonyls. Although the phenomenological explanation, given in ref. [1a], is consistent with our model, we do not completely agree with details for several reasons. As we allow orbital specific configuration interaction, we are not forced to assume equal energy separations between satellite and main peaks for all ligand orbitals. Additionally it has to be underlined that configurations, already essential in the pure ligand, must be included. Thus to come to an understanding of manybody effects in coordinated systems, one has to take into account charge transfer excitations as well as intra-ligand excitations.

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## Appendix

The appendix compiles the numerical data, used to discuss the many-body effects. The results are listed in the same sequence as referred to in the text. For

# Table 2 Characteristic data for carbon monoxide

Orbital	Loopmans energy by CNDO (eV)	Main inter- acting configuration	Configura- tion energy (eV)	Interaction matrix element (eV)
3σ	-45.3	$6\sigma 4\sigma^{-1}5\sigma^{-1}$ $2\pi 4\sigma^{-1}1\pi^{-1}$	39.8 38.8	1.0 1.7
4σ	-24.7	$\frac{2\pi 4\sigma^{-1}1\pi^{-1}}{2\pi 1\pi^{-1}5\sigma^{-1}}$	38.8 28.3	2.4 2.2
1π	-21.1	$ \begin{array}{c} 6\sigma 4\sigma^{-1}1\pi^{-1} \\ 6\sigma 1\pi^{-1}5\sigma^{-1} \\ 2\pi 1\pi^{-2} \end{array} $	45.9 36.1 35.2	1.3 1.3 2.4
5σ	-17.3	$\frac{6\sigma 4\sigma^{-1} 5\sigma^{-1}}{2\pi 4\sigma^{-1} 1\pi^{-1}}$ $\frac{2\pi 1\pi^{-1} 5\sigma^{-1}}{2\pi 1\pi^{-1} 5\sigma^{-1}}$	39.8 38.8 28.3	1.3 2.2 1.0

Table 3 Characteristic data for nitrogen

Orbital	Koopmans energy by CNDO (eV)	Main inter- acting configuration	Configura- tion energy (eV)	Interaction matrix element (eV)
3σ	-43.2	$6\sigma 4\sigma^{-1}5\sigma^{-1}$ $2\pi 4\sigma^{-1}1\pi^{-1}$	42.0 35.6	1.2 1.9
4σ	-25.2	$6\sigma 5\sigma^{-2}$ $2\pi 1\pi^{-1}5\sigma^{-1}$	35.2 28.7	1.3 2.4
$1\pi$	-20.3			
5σ	-18.3	$2\pi 4\sigma^{-1}1\pi^{-1}$	35.6	2.4





Orbital	Koopmans energy by CNDO (eV)	Main inter- acting configuration	Configura- tion energy (eV)	Interaction matrix element (eV)
3σ	-45.1	$\frac{2\pi 3\sigma^{-1}\pi_{M}^{-1}}{6\sigma 4\sigma^{-1}5\sigma^{-1}}$ $\frac{2\pi 4\sigma^{-1}\pi^{-1}}{2\pi 4\sigma^{-1}\pi^{-1}}$	44.0 43.0 39.6	2.3 1.0 1.7
4σ	25.2	$S_{M}4\sigma^{-1}5\sigma^{-1}$ $2\pi4\sigma^{-1}1\pi^{-1}$ $2\pi1\pi^{-1}5\sigma^{-1}$ $2\pi4\sigma^{-1}\pi_{M}^{-1}$ $2\pi5\sigma^{-1}\pi_{M}^{-1}$	46.2 39.6 32.0 24.7 19.8	1.8 1.7 2.2 2.2 1.2
1π	-21.4	$S_{M}1\pi^{-1}5\sigma^{-1}$ $6\sigma^{-1}1\pi^{-1}5\sigma^{-1}$ $2\pi1\pi^{-2}$ $2\pi1\pi^{-1}\pi_{M}^{-2}$	43.0 39.1 36.4 20.5	2.0 1.1 1.9 2.4
5σ	-19.1	$S_{M}4\sigma^{-1}5\sigma^{-1}$ $6\sigma4\sigma^{-1}5\sigma^{-1}$ $2\pi4\sigma^{-1}1\pi^{-1}$ $S_{M}5\sigma^{-2}$ $2\pi4\sigma^{-1}\pi_{M}^{-1}$ $2\pi5\sigma^{-1}\pi_{M}^{-1}$	46.2 43.1 39.6 38.7 24.7 19.8	1.5 1.3 2.2 1.5 1.3 1.8
δ <sub>M</sub>	-9.8	$ S_{M} 4\sigma^{-1} \delta_{M}^{-1}  2\pi \delta_{M}^{-1} \pi_{M}^{-1}  2\pi 1\pi^{-1} \delta_{M}^{-1}  S_{M} \delta_{M}^{-1} $	26.5 22.5 20.3 13.1	1.0 2.2 1.4 1.9
π <sub>M</sub>	-9.5	$2\pi 1\pi^{-2} \\ S_{M} 5\sigma^{-1}\pi_{M}^{-1} \\ 2\pi\pi_{M}^{-1} \\ 2\pi 1\pi^{-1}\pi_{M}^{-1} \\ S_{M}\pi_{M}^{-1}\sigma_{M}^{-1} $	36.4 21.4 20.8 20.5 12.5	1.4 1.3 1.8 1.5 1.8
σ <sub>M</sub>	-8.0	$ \begin{array}{c} \mathbf{S}_{\mathbf{M}} 5 \boldsymbol{\sigma}^{-1} \boldsymbol{\sigma}_{\mathbf{M}}^{-1} \\ 2 \pi 1 \pi^{-1} \boldsymbol{\sigma}_{\mathbf{M}}^{-1} \\ 2 \pi \pi \mathbf{M}^{-1} \boldsymbol{\sigma}_{\mathbf{M}}^{-1} \\ \mathbf{S}_{\mathbf{M}} \boldsymbol{\sigma}_{\mathbf{M}}^{-2} \end{array} $	20.1 18.8 18.5 11.0	1.2 1.3 1.8 1.3

Table 4			
Characteristic data	for	linear	Ni-CO

every molecule, we present a table of the most important intermixing configurations, their energies according to eq. (8), and the interaction matrix elements between the Koopmans state and the cited configuration. Additionally the graphical solution of the Dyson equation, with  $\Sigma(\omega)$  in the form of eq. (5), is given for the case of CO in fig. 12. Similar plots for the other cases are available on request.

Orbital	Koopmans energy by CNDO (eV)	Main inter- acting configuration	Configu- ration energy (eV)	Interaction matrix element (eV)
3σ	43.6	$ \begin{array}{r} 6\sigma 4\sigma^{-1}5\sigma^{-1} \\ 2\pi 3\sigma^{-1}\pi_{M}^{-1} \\ 2\pi 4\sigma^{-1}1\pi^{-1} \end{array} $	44.6 42.5 36.7	1.3 1.7 1.9
4σ	-26.8	$2\pi 1\pi^{-1} 5\sigma^{-1} 2\pi 4\sigma^{-1} \pi_{\overline{M}}^{-1} 2\pi 5\sigma^{-1} \pi_{\overline{M}}^{-1} $	29.8 26.4 19.2	2.3 1.6 1.3
1π	20.9	$\frac{SM1\pi^{-1}5\sigma^{-1}}{2\pi1\pi^{-1}\pi_{M}^{-1}}$ $\frac{2\pi\pi\pi_{M}^{-2}}{2\pi\pi_{M}^{-2}}$	44.6 20.1 24.3	1.6 1.7 1.1
5σ	-20.0	$\begin{array}{c} 6\sigma 4\sigma^{-1} 5\sigma^{-1} \\ S_{M} 5\sigma^{-2} \\ 2\pi 4\sigma^{-1} 1\pi^{-1} \\ 2\pi 4\pi^{-1} \pi_{M}^{-1} \\ 2\pi 5\sigma^{-1} \pi_{M}^{-1} \end{array}$	44.6 44.0 36.7 26.4 19.2	1.4 1.3 2.3 1.3
δ <sub>M</sub>	-10.6	$\frac{S_M 4 \sigma^{-1} \delta_M^{-1}}{2 \pi \delta_M^{-1} \pi_M^{-1}} \frac{S_M 5 \sigma^{-1} \delta_M^{-1}}{S_M 5 \sigma^{-1} \delta_M^{-1}} \frac{2 \pi 1 \pi^{-1} \delta_M^{-1}}{S_M \delta_M^{-1} \delta_M^{-1}}$	27.7 25.7 20.9 20.5	1.2 1.9 1.4 1.6
π <sub>M</sub>	-10.3	$S_{M}\sigma_{M}\sigma_{M}$ $S_{M}4\sigma^{-1}\pi_{M}^{-1}$ $2\pi\pi_{M}^{-2}$ $S_{M}5\sigma^{-1}\pi_{M}^{-1}$ $2\pi1\pi^{-1}\pi_{M}^{-1}$ $S_{M}\pi_{M}^{-1}\delta_{M}^{-1}$	28.2 24.3 21.5 20.1 10.9	1.8 1.2 1.6 1.3 1.6 1.8
σ <sub>M</sub>	-8.0	$\begin{array}{c} & M & M & M \\ & 6\sigma 3\sigma^{-1}\sigma_{M}^{-1} \\ & S_{M}5\sigma^{-1}\sigma_{M}^{-1} \\ & 2\pi\pi_{M}^{-1}\sigma_{M}^{-1} \\ & 2\pi 1\pi^{-1}\delta_{M}^{-1} \\ & S_{M}\sigma_{M}^{-2} \end{array}$	49.3 20.7 19.8 17.9 9.3	1.3 1.1 1.5 1.5 1.2

## Table 5 Characteristic data for linear Ni-N<sub>2</sub>

## Table 6

Characteristic data for bridged Ni-N2

Orbital	Koopmans energy by CNDO (eV)	Main inter- acting configuration	Configura- tion energy (eV)	Interaction matrix element (eV)
3σ	-44.4	$2\pi 3\sigma^{-1}\pi_{M}^{-1}$	45.5	1.8
		$6\sigma 4\sigma^{-1} 5\sigma^{-1}$	42.5	1.2
		$2\pi 4\sigma^{-1}1\pi^{-1}$	38.9	1.6
		$2\pi 4\sigma^{-1}1\pi^{-1}$	36.4	1.6

Orbital	Koopmans energy by CNDO (eV)	Main inter- acting configuration	Configura- tion energy (eV)	Interaction matrix element (eV)
4σ	-25.3	$S_{M}4\sigma^{-1}1\pi^{-1}$	49.4	1.7
		$6\sigma 5\sigma^{-2}$	35.7	1.3
		$2\pi 1\pi^{-1}5\sigma^{-1}$	32.1	1.9
		$2\pi 1\pi^{-1}5\sigma^{-1}$	29.6	2.0
		$2\pi 4\sigma^{-1}\pi_{M}^{-1}$	26.3	1.9
		$2\pi 1\pi^{-1}\sigma_{\rm M}^{-1}$	19.4	1.0
		$2\pi 5 \sigma^{-1} \pi_{\rm M}^{-1}$	18.8	1.0
$1\pi$	-21.4	$2\pi 1\pi^{-1}\pi_{M}^{-1}$	23.0	1.6
		$2\pi 1\pi^{-1}\pi_{M}^{-1}$	21.6	1.3
1π	-20.8	$S_{M}1\pi^{-1}\pi_{M}^{-1}$	23.2	1.0
		$2\pi 1\pi^{-1}\pi_{M}^{-1}$	22.1	1.8
		$2\pi\pi \overline{M}^2$	21.9	1.2
5σ	-18.5	$S_M 1 \pi^{-1} 5 \sigma^{-1}$	42.6	1.7
		$6\sigma 4\sigma^{-1} 5\sigma^{-1}$	42.5	1.5
		$2\pi 4\sigma^{-1}1\pi^{-1}$	38.9	1.9
		$2\pi 4\sigma^{-1}1\pi^{-1}$	36.4	2.0
		$2\pi 5\sigma^{-1}\pi_{\rm M}^{-1}$	19.5	1.9
δ <sub>M</sub>	-10.2	$S_M 1 \pi^{-1} \delta_M^{-1}$	23.3	1.4
		$2\pi\delta_{\mathrm{M}}^{-1}\pi_{\mathrm{M}}^{-1}$	22.9	1.8
		$S_M \delta_M^{-1} \delta_M^{-1}$	11.8	1.9
δ <sub>M</sub>	-10.1	$S_M 1 \pi^{-1} \delta_M^{-1}$	23.2	1.4
		$2\pi\delta_{M}^{-1}\pi_{M}^{-1}$	22.9	1.8
		$S_M \delta_M^{-1} \delta_M^{-1}$	11.7	1.9
$\widetilde{\pi}_{M}$	-9.9	$2\pi \pi_{M}^{-1} \delta_{M}^{-1}$	32.6	1.3
		$S_{M}1\pi^{-1}\pi_{M}^{-1}$	24.4	1.2
		$2\pi\pi M^{-2}$	21.1	1.3
		$SMk_M^{-1}\sigma_M^{-1}$	11.5	1.8
$\widetilde{\pi}_{M}$	-9.6	$S_M 1 \pi^{-1} \pi_M^{-1}$	23.2	1.3
		$2\pi 1\pi^{-1}\pi_{\rm M}^{-1}$	22.1	1.2
		$2\pi \pi_{\rm M}^{-2}$	21.9	1.7
		$S_M \pi_M^{-1} \delta_M^{-1}$	11.2	1.9
σ <sub>M</sub>	-7.8	$S_M 1 \pi^{-1} \sigma_M^{-1}$	22.7	1.0
		$2\pi\pi \widetilde{M}^{1}\delta \widetilde{M}^{1}$	18.3	1.4
		SM <sup>8</sup> M <sup>2</sup>	9.6	1.3

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