PHYSICAL REVIEW B VOLUME 20, NUMBER 12 15 DECEMBER 1979

Theoretical calculation of bonding, shakeup energies, and shakeup intensities in $Ni(CO)_4$

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(Received 6 August 1979)

We report the results of first-principles calculations of shakeup energies and shakeup intensities for the photoelectron spectra of carbonyls. The bonding of CO in $Ni(CO)_4$ and the mechanism by which core holes produced by the photoexcitation are screened are discussed. The calculations are based on the self-consistent-field (SCF)-$X\alpha$ multiple-scattering theory.

In recent years a great deal of attention has been devoted to studying the changes in the core-hole photoemission spectra of small molecules and atoms when they are chemisorbed on transition metal surfaces.[1,2] There are two major effects of interest: (i) shifts in the binding energy of the core electrons and (ii) the appearance of satellite peaks associated with excited states of the ion. The self-consistent atom-jellium model[1] suggests that in some cases the screening of the core hole is affected by the occupation of an originally empty adsorbate level which drops below the Fermi energy owing to the attraction of the core-hole potential. Model calculations[2] show that this screening mechanism is capable of reproducing the satellite structure obtained in the spectra of CO adsorbed on metal surfaces.

Experiments[3-6] on transition-metal carbonyl complexes show that the photoelectron spectra of carbonyl containing a single metal atom exhibits all the qualitative features seen in the spectra of adsorbed CO and that multimetal carbonyl spectra are in quantitative agreement with that of adsorbed CO.[3] In addition, for every CO-derived peak in the carbonyl spectra there is a satellite structure at ~6 eV higher binding energy with an intensity of 20% to 30% (depending on the molecule) of the parent peak.[3,5] Finally, it has been shown that the screening of holes created in photoemission is almost as effective in $Cr(CO)_6$ as in adsorbed CO.[4]

The objective of this paper is to understand the screening process and the satellite structure in carbonyls. The approach is novel in that the results are free of adjustable parameters. This type of calculation has not yet been carried out for carbonyls, where all interatomic distances are known, due to the numerical difficulties involved. For this reason we have used a simple one-electron theory as our starting point: the self-consistent-field (SCF)-$X\alpha$-multiple-scattering technique.[6] The results shed light on the bonding of CO in $Ni(CO)_4$, the screening of core holes in photoemission, and ascribe the satellite in carbonyls to a 1π to 2π transition. The latter is done by obtaining excellent agreement with experiment for *both* the calculated shakeup energies and shakeup intensities. This calculation and the resultant understanding of the carbonyl spectra furnish a test system with which parametrized calculational schemes may be compared.

The term shakeup refers to photoexcitation processes in which the residual ion is in an excited state. This is illustrated in Fig. 1, which is based on an independent-particle description of the ion. There, the peaks in the photoemission spectra are interpreted as arising from either a one- or a two-electron event. The kinetic-energy position (E_k) of a peak (i) in the spectrum is given by

$$E_k(i)=E_0+h\omega-E(i)\,, \qquad (1)$$

where E_0 is the ground-state energy of the neutral molecule, $h\omega$ is the photon energy, and $E(i)$ is the energy of the ion in its ith excited state. Note that since only $E_k(i)$ and $h\omega$ are measured experimentally, we know only differences between $E(i)$'s. When one refers to a satellite and its main peak, this difference is labeled the shakeup energy. Our calculation of shakeup intensities was done using the sudden-approximation[7,8] method. The basic approximation made is that the N-electron wave function of the neutral molecule can be written as

$$\psi_{\text{neutral}}(N)=\phi_j(1)\psi_j{}^R(N-1)\,, \qquad (2)$$

where $\phi_j(1)$ is the molecular-orbital wave function of the core state (labeled j) from which the electron is photoejected and $\psi_j^R(N-1)$ is the properly antisymmetrixed remainder function constructed from the rest of the occupied molecular orbitals. Two other assumptions are made. First, that $\phi_j(1)$ is orthogonal to all occupied molecular orbitals of the ion ($\tilde{\phi}_i$):

$$\int \tilde{\phi}_i(1)^*\phi_j(1)d\tau_1=0\,. \qquad (3)$$

Second, that if the kth molecular orbital of the ion

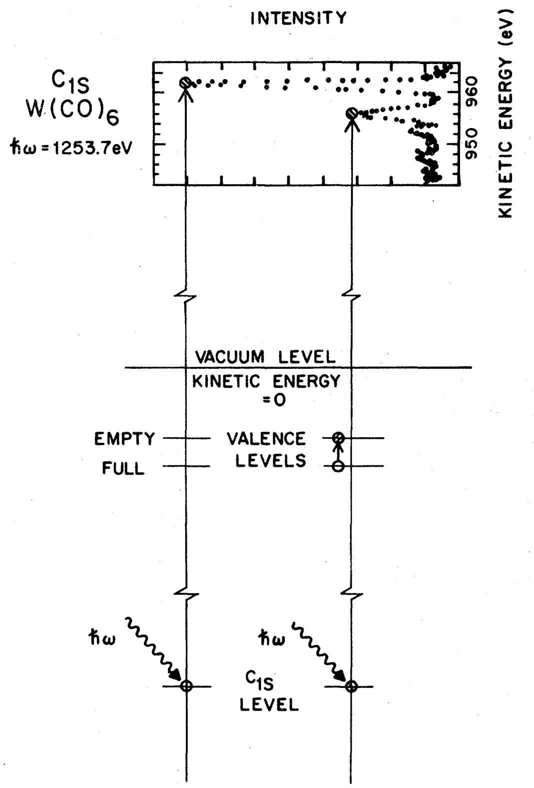

FIG. 1. Above, the C_{1s} region of the photoelectron spectra of $W(CO)_6$ excited with Mg $K\alpha$ radiation from Ref. 3. Below, an interpretation of the peaks in a one-electron picture.

describes the photoemitted electron,

$$\int \tilde{\phi}_i(1)^*(\hat{A}\cdot\hat{P}_1)\phi_j(1)d\tau_1 \approx \delta_{1,k} f_{kj} . \tag{4}$$

In other words, this means that the photoemission operator couples core levels and continuum levels more effectively than it couples core levels and bound states. This is true for high kinetic energies of the ejected electron.

From these approximations it can be shown that the photoemission matrix element which couples the wave function of the neutral to a given state of the ion is given by

$$M \propto \int \tilde{\phi}_k(1)\hat{A}\cdot\hat{P}_1\phi_j(1)d\tau_1 \times \int \psi_{ij}^{\text{ion}}(N-1)\psi_j^R(N-1)d\tau . \tag{5}$$

In Eq. (5), $\tilde{\phi}_k$ is the molecular orbital of the ion that describes the photoemitted electron and ψ_{ij}^{ion} is the wave function of the ion in its *i*th excited state after the creation of a core-hole j. Note that Eq. (5) implies that one can split the calculation of shakeup intensities into two parts. First, the calculation of the one-electron integral. The square of this integral is proportional to the total photoemission intensity. The intensity is distributed between the main peak and its satellites. This distribution of the total weight is governed by the square of the $(N-1)$-electron integral of Eq. (5). Thus, we only calculate the $(N-1)$-electron integral whose square we call P_{ij}: the probability that photoemission from a core-level j leaves an ion in its *i*th excited state.

It is important to note that in Eq. (5), ψ_j^R and ψ_{ij}^{ion} are antisymmetrized $(N-1)$-electron wave functions. The integration in Eq. (5) runs over their spin and space coordinates. In some cases[9] a one-electron integral may approximate P_{ij}. In general, and in particular for $Ni(CO)_4$, Eq. (5) must be used.

Also note that if the set of functions ψ_{ij} form a complete orthogonal set, the sum over i of the probabilities P_{ij} will be unity. In the calculations shown below we have such orthogonality.[10] In general, since the states of the ion are calculated using different self-consistent potentials, this orthogonality is not guaranteed.

This paper is divided into five parts. First, we describe the calculation and its application to the neutral ground state of $Ni(CO)_4$. The resultant picture of bonding in carbonyls is discussed. Second, we investigate the behavior of the system as we create a core hole. This yields a description of the relaxation–core-hole screening process. Third, we discuss other excited states of the ion. Specifically, we obtain the energy differences between excited ionic states and the molecule with one core hole. This gives shakeup energies for different transitions which are compared to the experimental data. Fourth, we calculate shakeup intensities and compare them to experimental intensities. Finally, similar calculations for carbon monoxide are discussed.

We proceed to discuss the electronic structure of $Ni(CO)_4$ in its ground state. In the gas phase this molecule has T_d symmetry. It is well established that, for photoemission from core levels in a molecule like $Ni(CO)_4$, the ion is best described by localizing the hole in one of the CO molecules.[11] Thus, all calculations were performed using C_{3v} symmetry: one CO has been considered different from the other three. Even though we will use the chemical formula $Ni(CO)_4$, the proper one would be $Ni(CO)_3CO$. Thus, for every CO-derived σ symmetry level, we obtain two a_1 levels and one doubly degenerate e level. As will be shown, the breaking of the symmetry for the neutral molecule has a small effect. In the example above, it implies that one of the two a_1 levels is almost degenerate with the e level.

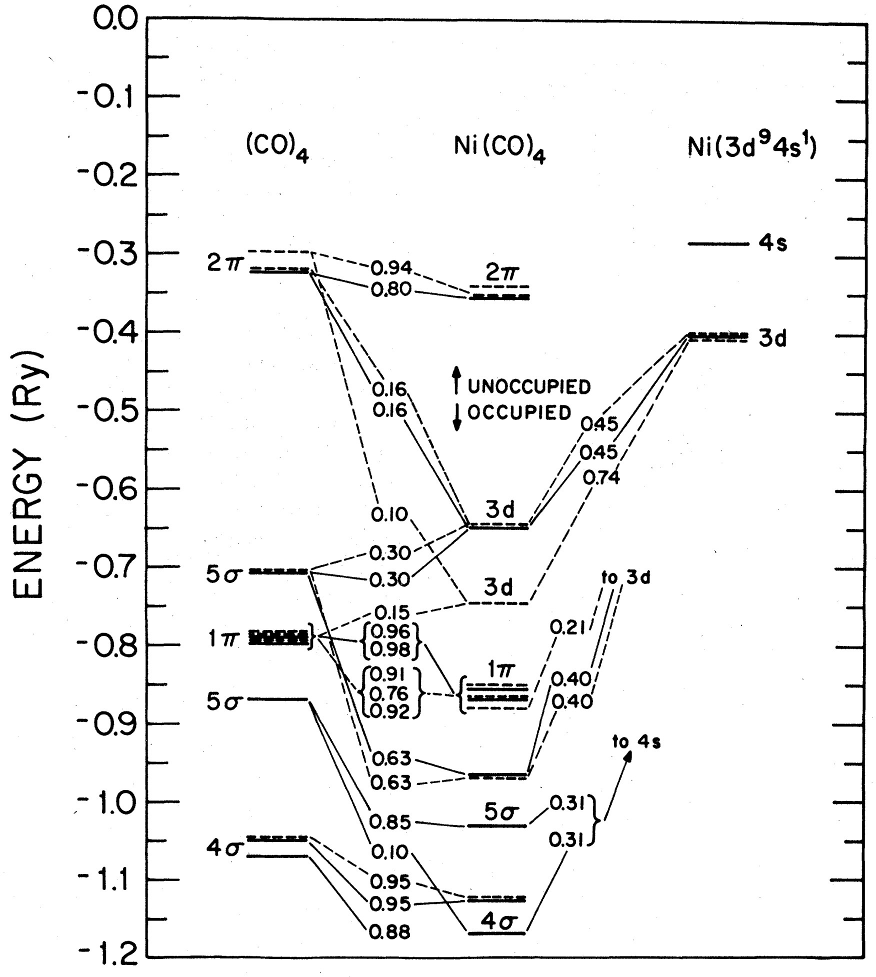

FIG. 2. Energy eigenvalues of the orbitals of $(CO)_4$, $Ni(CO)_4$ and $Ni(3d^9 4s^1)$. Labeled in terms of their main CO or Ni character. Also shown are all the squares of overlaps which are larger than 0.10. Levels of e symmetry are labeled by dashed lines, those of a_1 and a_2 symmetry are labeled by full lines. Parameters used in the calculation are shown in Table I.

The splitting observed is numerical in nature and small enough to be of no concern. The calculated energy eigenvalues of the valence levels of $Ni(CO)_4$ are shown in Fig. 2 (see Table I also). The levels are labeled in terms of their main CO or Ni character. Also shown in Fig. 2 are the energy eigenvalues of the Ni atom and the hypothetical molecule $(CO)_4$. Figure 2 also shows all squares of overlaps of wave functions of $Ni(CO)_4$ with those of Ni and $(CO)_4$. The overlap O_{ij} between eigenfunctions $\phi_i(\vec{r})\phi_j(\vec{r})$ of $Ni(CO)_4$ and $(CO)_4$, respectively, is defined as

$$O_{ij} = \int \phi_i^*(\vec{r})\phi_j(\vec{r})\,d\vec{r} \,. \qquad (6)$$

It is calculated using numerical integration within the muffin tins and via Green's theorem in the intersphere region. These overlaps provide an orbital decomposition similar to the one effected in Hartree-Fock–linear-combination-of-atomic-orbitals (HF-LCAO) calculations.[12] It is clear that the 1σ, 2σ, 3σ, 4σ, and 1π manifolds of levels are basically unaltered by bonding. The 5σ, 2π,

TABLE I. Parameters used in SCF-$X\alpha$–muffin-tin–multiple-scattering calculations of $Ni(CO)_4$. The calculations on $(CO)_4$ and Ni use the same sphere radii and distances as above but values of α for outer, empty, and intersphere regions differ.

Distances in a.u.	Radii in a.u.	Values of α
$D_{Ni-C} = 1.818$	$R_{Ni} = 1.98$	$\alpha_{Ni} = 0.7087$
$D_{C-O} = 1.149$	$R_C = R_{C'} = 0.620$	$\alpha_C = \alpha_{C'} = 0.759$
	$R_O = R_{O'} = 0.529$	$\alpha_O = \alpha_{O'} = 0.744$
	$R_{outer} = 3.496$	$\alpha_{outer} = \alpha_{int} = 0.7274$

and d levels mix, giving rise to bonding and antibonding levels. This is best shown by the following expansion of the eigenfunctions of $Ni(CO)_4$ in terms of those of Ni and $(CO)_4$. Labeling the levels by their main character and energy eigenvalues, for the $Ni(CO)_4$ levels involved in the bonding of the above decomposition, yields

$$|d(-0.65)\rangle_e = -0.67\,|d\rangle - 0.54\,|5\sigma\rangle + 0.40\,|2\pi\rangle\ ,$$

$$|d(-0.65)\rangle_{a_1} = +0.67\,|d\rangle - 0.55\,|5\sigma\rangle + 0.39\,|2\pi\rangle\ ,$$

$$|5\sigma(-0.97)\rangle_e = 0.52\,|d\rangle + 0.79\,|5\sigma\rangle\ ,$$

$$|5\sigma(-0.97)\rangle_{a_1} = 0.52\,|d\rangle + 0.79\,|5\sigma\rangle\ ,$$

while for other levels

$$|d\,(-0.74)\rangle_e = 0.86\,|d\rangle + 0.31\,|2\pi\rangle - 0.38\,|1\pi\rangle,$$

$$|5\sigma(-1.03)\rangle_{a_1} = 0.92\,|5\sigma\rangle\ ,$$

$$|4\sigma(-1.12)\rangle_e = 0.97\,|4\sigma\rangle\ ,$$

$$|3\sigma(-1.97)\rangle_e = 0.99\,|3\sigma\rangle\ .$$

Thus, it is clear that d levels mix predominantly with the 5σ levels to form bonding orbitals at −0.97 Ry and antibonding orbitals at −0.74 Ry. The latter shows 45% d character, 29% 5σ, and 16% 2π character.

The amount of 2π mixing in carbonyls has been a subject of considerable attention. Different calculational schemes produce different estimates of this number. The Hartree-Fock-LCAO[5] and discrete-variational-$X\alpha$[13] methods both yield about the same amount of mixing as is predicted here. On the contrary, SCF-$X\alpha$ calculations with overlapping spheres[14] predict a predominant σ bond with small π interaction. These latter results are mainly based on the interpretation of charge-density plots and not on the analysis of overlap integrals. For this reason we believe they overemphasize σ bonding vs π bonding.

Once we understand the electronic structures of neutral $Ni(CO)_4$ in its ground state, we proceed to study the effect of creating a core hole. This hole is localized in one of the CO moieties as is indicated by the chemical formula $Ni(CO)_3(CO^+)$. Figure 3 shows the energy eigenvalues of such a molecule with a 2σ core hole and includes squares of overlaps with the neutral-molecule wave functions. To first order, the major difference between the neutral molecule and the ion is the degree of localization of the wave functions. Whereas in the neutral all orbitals were delocalized over the four CO moieties, in the ion one can distinguish both in their eigenvalues and in their charge distributions two types of eigenfunctions. Some are essentially localized to the CO where the hole is, and the rest are delocalized over the other three CO's or at the Ni atom. We will refer to levels as being localized or delocalized. As expected, localized levels feel the attraction of the core hole more than the delocalized ones. On average the localized levels eigenvalues are 1.4 eV lower in energy than the delocalized levels.

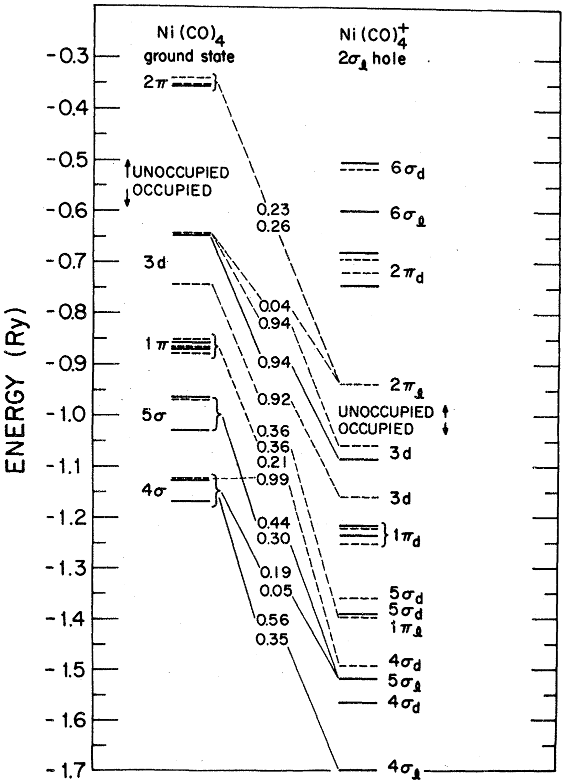

FIG. 3. Effect of a 2σ localized core hole is shown. On the left-hand side are eigenvalues of $Ni(CO)_4$; on the right-hand side are those of the ion with a 2σ localized hole. Only overlaps to localized levels or levels of the ion are shown. In the figure l and d label localized and delocalized, respectively.

The second most important change that occurs when the hole is created is the screening of the hole. Without screening, the number of electrons $N_{C'}$ in the carbon sphere where the hole is created (labeled C′) would decrease by 1.0. Since the system responds to the hole, there is screening: $N_{C'}$ changed from 3.83 in the neutral state to 3.91 in the ion, while the charge in the other carbon atoms did not change. Thus, the hole is more than totally screened within the carbon sphere. Where did the 1.07 screening electrons come from? We can get some idea by looking at charge depletion in other areas of the molecule: −0.73 in the intersphere region, −0.14 in the adjacent oxygen atom, and −0.09 in the Ni sphere. This implies that the screening is not carried out solely by the nickel-atom d levels but that other levels, mainly the localized ones, are involved. Specifically, the localized 1π level changes and adds 0.58 electrons in the carbon sphere; the localized 4σ and 3σ levels add 0.20 and 0.11 electrons, respectively, and the d levels add 0.09 electrons.

The model of screening obtained here disagrees with previous pictures. Rajoria *et al.*,[15] following Lang and Williams,[1] claim that, upon creation of the core hole, the localized 2π level drops below the occupied d levels, and screening is achieved by partially filling this level. To explain the shakeup structure they require that the 2π level be ~6 eV below the d levels. For their model to be correct our calculation has to be in error by ~9 eV in the relative position of the 2π and d levels. That is not possible. There is a second way to achieve occupancy of the 2π level[5]: if the d levels of the ion have more 2π character than the d levels of the neutral state. Again, our calculations do not bear this out. These two models are too simple. Our screening mechanism has also been found to be correct for a $Cu_5(CO)$ cluster.[16]

The above discussion on screening also applies to shakeup energies and intensities. As mentioned previously, the atom-jellium screening mechanism has been extended using model calculation[2] to describe shakeup energies and intensities. To the extent that no simple d-2π screening occurs, the shakeup mechanism is also complicated. The remainder of this paper will deal with the calculation of shakeup energies and intensities to identify the cause of the satellite structure. By shakeup energies we mean differences in the total energy of the ion in an excited state with respect to a calculation with one core hole. Again, we focus on a 2σ-level core hole. Starting with that configuration, the energy required to excite a d electron to a localized 2π level is calculated via the transition-state approach.[17] Thus, the d to 2π shakeup energy and other shakeup energies are calculated. The results are summarized in Table II. As is expected from energy differences of the eigenvalues of Fig. 3, shakeups from the d levels to the localized 2π level have small energies. It is impossible to attribute the d to 2π shakeup as the cause of the intense satellites at ~6 eV shakeup energy. On the other hand, high-resolution spectra of hexacarbonyls show a low-intensity peak at ~2 eV shakeup energy,[18] which is attributed to photoemission from the C_1 level of residual gas-phase CO. We believe that it corresponds to d to 2π shakeups of small intensity.

The localized 1π to 2π shakeup energy is in better agreement with the shakeup energy of the intense satellite. Given the intrinsic accuracy of the calculation, an "error" of ~0.3 eV corresponds to excellent agreement.

To further assure that a transition from the localized 1π level to the localized 2π level is the cause of the intense satellite peak in the core-hole spectra of carbonyls, we calculate the intensity of this and other shakeups. As explained before, we use Eq. (5) to calculate the probability of shakeup's occurring. The results of calculations of shakeup intensities are summarized in Table II. As mentioned previously, experimental data for carbonyls show a satellite of 20% to 30% intensity (depending on the molecule) at ~6 eV energy. We believe that the agreement of both intensity and energy assures that the 1π to 2π shakeup is responsible for the satellite structure in the core-hole spectra of carbonyls.

The 1π to 2π shakeup is not as prominent in the gas-phase CO spectrum.[19] Using the same procedure described above, we calculated the shakeup energy and intensity of the 1π to 2π shakeup in $(CO)_4$. We find, as shown in Table II, that in this hypothetical molecule this shakeup has only 2.5% of the strength of the main peak. This agrees well with the experimental value of 3.1%. Also of interest is the change in the size of the main peak. In $Ni(CO)_4$ the main peak has 61% of the total cross section; in $(CO)_4$ it has 81%. Provided the one-electron-photoemission matrix element remains unchanged on bonding, this implies a measurable reduction of 25% in the size of the main peak. The major difference between $(CO)_4$ and $Ni(CO)_4$ which accounts for their dissimilar satellite structure can be traced back to the 5σ-d bonding. The

TABLE II. Shakeup energies and intensities in $Ni(CO)_4$ and $(CO)_4$.

$Ni(CO)_4$	Shakeup	Excitation energy (eV)	Probability of excitation	% main peak
	Main peak	0	0.613	100
	$d_2 \rightarrow 2\pi$	1.97	0.003	0.4
	$d_1 \rightarrow 2\pi$	3.47	0.002	0.4
	$1\pi \rightarrow 2\pi$	6.31	0.084	13.7
$(CO)_4$				
	Main peak	0	0.810	100
	$1\pi \rightarrow 2\pi$	6.99	0.020	2.5

screening charge in $(CO)_4$ which screens the 2σ hole comes from the 1π, 5σ, 4σ, and 3σ levels which add 0.45, 0.15, 0.1, and 0.1 electrons, respectively, to the carbon sphere. Note that the 5σ level is involved in the screening, while this was not the case in $Ni(CO)_4$, since there it was involved in the bonding. For this reason the 1π level in $Ni(CO)_4$ took most of the screening load and was perturbed enough to allow intense 1π to 2π shakeups.

To conclude, this calculation, based on a one-electron theory, gives evidence for ascribing the satellite peak observed in carbonyls to a 1π to 2π shakeup, agrees in the picture of bonding with previous discrete-variational-$X\alpha$ calculations, and gives a picture of the screening process in which all localized CO levels try to screen the photohole.

ACKNOWLEDGMENTS

We wish to thank E. W. Plummer, J. R. Schrieffer, and P. Soven for interesting discussions. We acknowledge the monetary support of this work by the National Science Foundation through the Materials Research Lab Program under Grant No. DMR-76-80994 and the Gas Research Institute through Grant No. GRI-5010-362-0041. Roy Marshall and the crew at the David Rittenhouse Laboratory Computer Center were extremely helpful; our thanks to them.

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[1] N. D. Lang and A. R. Williams, Phys. Rev. B 16, 2408 (1977).

[2] K. Schonhammer and O. Gunnarson, Solid State Commun. 23, 691 (1977); O. Gunnarson and K. Schonhammer, *ibid.* 26, 147 (1978); Phys. Rev. Lett. 41, 1608 (1978).

[3] E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B 18, 1673 (1978).

[4] G. Loubriel and E. W. Plummer, Chem. Phys. Lett. 64, 234 (1979).

[5] M. Barber, J. A. Conner, and I. H. Hillier, Chem. Phys. Lett. 9, 570 (1971).

[6] K. H. Johnson, *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic, New York, 1973), Vol. 7, p. 143.

[7] R. Manne and T. Aberg, Chem. Phys. Lett. 7, 282 (1970).

[8] B. I. Lundqvist, Phys. Kondens. Mater. 9, 236 (1966).

[9] L. J. Aarons, M. F. Guest, and I. H. Hillier, in Proc. Chem. Soc. Lond. J. Faraday Trans. II 68, 1866 (1972), and Refs. 1 and 8 within.

[10] The integral shown in Eq. (5) between excited states of the ion and the ion and its ground state is in the three cases considered less than 0.02.

[11] P. S. Bagus and H. F. Schaefer, III, J. Chem. Phys. 56, 224 (1972). Also see Ref. 15.

[12] I. H. Hillier and V. R. Saunders, Mol. Phys. 22, 1025 (1971). Also see Ref. 15.

[13] E. J. Baerends and P. Ros, Mol. Phys. 30, 1735 (1975).

[14] K. Johnson and V. Wahlgren, Int. J. Quantum Chem. 6, 243 (1972); J. B. Johnson and W. G. Klemperer, J. Am. Chem. Soc. 99, 7132 (1977).

[15] D. Rajoria, L. Kovnat, E. W. Plummer, and W. R. Salaneck, Chem. Phys. Lett. 49, 64 (1977).

[16] R. P. Messmer (private communication).

[17] J. C. Slater, *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic, New York, 1972), Vol. 6, p. 1.

[18] G. H. Bancroft, B. D. Boyd, and D. K. Creber, Inorg. Chem. 17, 1008 (1978).

[19] T. A. Carlson, M. O. Krause, and W. E. Maddeman, J. Phys. 32, C4-76 (1971); R. W. Shaw, Jr. and T. D. Thomas, Chem. Phys. Lett. 14, 121 (1972); U. Gelius, J. Electron Spectrosc. Relat. Phenom. 5, 985 (1974).