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Theoretical K-shell ionization spectra of N_2 and CO by a fourth-order Green's function method

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A recently developed complete fourth-order Green's function method referred to as ADC(4) was used to calculate ionization energies and relative intensities of $1s$ hole states in N_2 and CO. Very accurate $1s$ electron binding energies and a good qualitative description of the shakeup spectra at low and medium energies have been obtained. For the $N1s$ and $C1s$ results comparison is made with previous large-scale configuration interaction treatments. New results are presented for the $O1s$ shakeup spectrum of CO. Here striking differences with respect to the $C1s$ spectrum are found which are explained in terms of charge–transfer effects induced by electronic excitation. We also present results for shakeup states of symmetries other than $^2\Sigma^+$ which are not observed in the usual photoemission experiment.

I. INTRODUCTION

Core-level photoelectron spectra of the "model" diatomic molecules N_2 and CO were first recorded at high resolution with monochromatized x-ray line sources over a decade ago.[1-3] The $N1s$ and $C1s$ ionization spectra of N_2 and CO, respectively, which may be viewed as typical for small unsaturated molecules, exhibit a strong satellite structure on the high binding energy side of the $1s$ single hole main state. About 30%–40% of the $1s$ partial photoionization cross section shows up in shakeup (and shake-off) states, where the core level vacancy is accompanied by a valence excitation (ionization). Of considerable spectral strength and at lowest energy are shakeup states involving $\pi-\pi^*$ excitations, i.e., electron promotions from occupied to unoccupied valence-type orbitals of π symmetry. The earlier experimental work has been recently augmented by synchrotron radiation experiments allowing—though still at modest spectral resolution—to trace the intensity variation of spectral peaks as a function of photon energy. Photon energy dependent cross sections of $1s$ single hole (main) states in N_2 and CO have been measured by Truesdale et al.[4] and Lindle et al.[5] An interesting intensity variation near threshold of the first and second $\pi-\pi^*$ shakeup state in the $C1s$ spectrum of CO was reported recently by Reimer et al.[6] With respect to the $O1s$ shakeup region in CO, the experimental situation was far less satisfactory for many years, since the available spectra were of very low resolution.[7,8] Only recently, a high resolution $O1s$ shakeup spectrum of CO has been recorded showing a surprising difference with respect to its $C1s$ counterpart.[9]

Previous theoretical work on K-shell ionization in N_2 and CO includes ΔSCF[10-14] and transition operator[15,16] calculations of core-level binding energies, limited[17,18] and large scale[19-22] configuration interaction (CI) treatments for $1s$ hole main and shakeup states, and calculations of par-

tial $1s$ photoionization cross sections.[23-26] The ionization energies of $1s$ hole main states ($1s$ electron binding energies) are usually quite satisfactorily described on the ΔSCF level, i.e., by separate Hartree–Fock (HF) calculations for the initial (neutral) ground state and the ionic $1s$ hole state. Hereby one takes into account the relaxation of the valence electrons in the presence of the core-level vacancy which is the major correction to the first-order (Koopman's) result-ϵ_{1s} for the $1s$ binding energy corresponding to unrelaxed (frozen) orbitals. For N_2 and CO the best ΔSCF results agree with the experimental $N1s$, $C1s$, and $O1s$ binding energies, respectively, up to ± 1 eV, where, as is well known, the $N1s$ case requires a localized SCF representation of the cation.[27] To improve the theoretical description one has to account for electron correlation, e.g., by performing CI calculations for the neutral ground and final ionic state. Employing large-scale CI expansions Butscher et al.[21] have obtained a very accurate result for the $N1s$ binding energy in N_2.

With the exception of the work of Butscher et al.[21] the previous CI studies of K-shell ionization in N_2 and CO aimed not to determine absolute binding energies but rather to calculate shakeup energies and relative intensities. Whereas the early limited CI expansions[17,18] turned out to be quite insufficient, a good theoretical description of low energy shakeup states was obtained by large-scale CI treatments[19-22] of $N1s$ and $C1s$ ionization of N_2 and CO, respectively. These studies clarified and confirmed, in particular, the assignment of the first and second shakeup peak at 8.3 and 14.9 eV excitation energy in the $C1s$ spectrum of CO and of similar structure in the case of N_2, as being due to two distinct $\pi-\pi^*$ states differing with respect to the intermediate spin $S' = 1$ and 0 of the open π shells. Similar to the experimental situation, the $O1s$ shakeup spectrum of CO has hitherto escaped a comparable theoretical scrutiny: we are not aware of any large-scale CI study of this case.

As an alternative theoretical approach to atomic and molecular ionization spectra, the method of the one-particle

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Green's function (electron propagator) and related many-body methods have been used with considerable success.[28-31] These methods have the conceptual advantage that the relevant physical information, ionization energies, and relative spectral intensities can be calculated directly, without resorting to separate calculations for the (neutral) initial and final ionic states. Previous calculations, employing approximation schemes consistent through third order in the electronic repulsion, gave very accurate results for outer valence single-hole (main) states and a good qualitative description of shakeup states and of the inner-valence region where, due to strong mixing of single-hole and shakeup states, the familiar one-particle picture of ionization may break down.[32] The third-order approximation schemes, however, turned out to be insufficient for applications to the regime of core-level ionization since the large relaxation shifts for the $1s$ main states and even more for the shakeup states are not properly accounted for. For N_2 and CO the third-order results of $1s$ main and satellite energies exceed the experimental values by 3–5 and 6–10 eV, respectively.

Extensions of the third-order level by including selected fourth-order terms have been proposed and tested by Redmon et al.,[33] Hermann et al.,[34] and Baker.[35] Of these authors only Baker has considered the case of core-level ionization, but his results for the O$1s$ and C$1s$ binding energies of H_2O and C_2H_4, respectively, do not show a convincing improvement. A complete fourth-order approximation scheme to the one-particle Green's function G has recently been derived within the framework of diagrammatic perturbation theory.[36] This approximation, referred to as fourth-order algebraic diagrammatic construction [ADC(4)], allows for an infinite summation complete through fourth order of the perturbation expansion for G. Within this scheme the ionization energies and spectroscopic factors are obtained as eigenvalues and eigenvector components, respectively, of a Hermitean secular matrix. In general, the numerical effort required for constructing and diagonalizing the ADC(4) secular matrix is considerable and prevents for the moment a straightforward application to the valence ionization of all but the smallest systems. The restriction to the case of K-shell ionization, however, allows a very effective reduction of the ADC(4) equations: here one may neglect to a good approximation the correlation of core and valence electrons yielding a decoupled secular problem of tractable size. In this paper we describe the first application of the ADC(4) in calculations of the $1s$ ionization in N_2 and CO. Our study is intended to complement previous theoretical work on N$1s$(N_2) and C$1s$(CO) and to provide a theoretical description of the strikingly different O$1s$ shakeup spectrum in CO which apparently has not been recognized before. A preliminary report on our O$1s$ results together with a presentation of the newly recorded experimental spectrum by Svensson, Nordfors, and Gelius appeared elsewhere.[9] We also present results of core-hole states of symmetries other than $^2\Sigma^+$, which normally are not observed in the photoemission experiment.

The plan of this article is as follows: In Sec. II we give a brief presentation and discussion of the theoretical method. Details of the present calculations are specified in Sec. III. A discussion of our results is presented in Sec. IV, and some remarks concerning the performance of the ADC(4) method are found in Sec. V. Section VI contains a summary and conclusions.

II. THEORY

In the following we give a brief description of the Green's function method and of the ADC(4) approximation scheme employed in the present study. The derivation of the ADC(4) equations and a detailed discussion has been presented elsewhere.[36] For an overview of the Green's function approach to the calculation of atomic and molecular ionization spectra the reader is referred to review articles.[28-32]

A. One-particle Green's function

The one-particle Green's function for an atom or molecule in the ground state $|\Psi_0^N\rangle$ is defined as the matrix G of functions[37,38]

$$G_{pq}(t,t') = -i\langle\Psi_0^N|\hat{T}c_p(t)c_q^\dagger(t')|\Psi_0^N\rangle, \tag{1}$$

where $\hat{T}$ is Wick's time-ordering operator, and $c_q^\dagger(t)$ $[c_q(t)]$ denote creation (destruction) operators in the Heisenberg notation corresponding to the one-particle states $|\varphi_q\rangle$ [usually ground state Hartree–Fock (HF) states], and fulfilling the usual anticommutation relations. The physical content of G is apparent in the spectral representation[37,38]

$$G_{pq}(\omega) = \sum_n \frac{x_p^{(n)}x_q^{(n)*}}{\omega + E_n^{N-1} - E_0^N - i\eta}$$
$$+ \sum_n \frac{x_p^{(n)}x_q^{(n)*}}{\omega + E_0^N - E_n^{N+1} + i\eta}, \tag{2a}$$

$$x_p^{(n)} = \begin{cases} \langle\Psi_n^{N-1}|c_p|\Psi_0^N\rangle, & n\in\{N-1\} \\ \langle\Psi_0^N|c_p|\Psi_n^{N+1}\rangle, & n\in\{N+1\} \end{cases} \tag{2b}$$

Here, E_0^N is the ground state energy of the initial N-electron system; $|\Psi_n^{N\pm1}\rangle$ and $E_n^{N\pm1}$ denote eigenstates and energies of the systems having one electron more or less, respectively. The positive infinitesimal η in the denominators on the right-hand side of Eq. (2a) is required for the convergence of the Fourier transform between the time and energy representation of G. According to Eq. (2a) the (vertical electronic) ionization energies

$$I_n = E_n^{N-1} - E_0^N \tag{3a}$$

and electron affinities

$$A_n = E_0^N - E_n^{N-1} \tag{3b}$$

are (up to the sign) given by the pole positions of $G(\omega)$. The amplitudes $x_p^{(n)}$ of the corresponding residues [Eq. (2b)] referred to as transition amplitudes or spectroscopic amplitudes are relevant for the bound state contribution to the spectral intensities. In the case of K-shell photoionization considered in this study the relative intensities for the production of $1s$ hole states are given by the spectroscopic factors

$$|x_{1s}^{(n)}|^2 = |\langle\Psi_n^{N-1}|c_{1s}|\Psi_0^N\rangle|^2 \tag{4}$$

if the conditions of the sudden limit,[39] i.e., the limit of high photon energy apply.

B. The algebraic–diagrammatic construction (ADC) for the self-energy

The usual approach for calculating $G(\omega)$ is to introduce an appropriate approximation for the self-energy $\Sigma(\omega)$ related to $G(\omega)$ via the Dyson equation[37,38]

$$G(\omega) = G^0(\omega) + G^0\Sigma(\omega)G(\omega). \qquad (5)$$

Here, $G^0(\omega)$ is the free Green's function defined with respect to the diagonal one-particle (HF) part of the Hamiltonian and the corresponding HF ground state. The explicit representation reads

$$G^0_{pq}(\omega) = \delta_{pq}\left(\frac{n_p}{\omega - \varepsilon_p - i\eta} + \frac{\bar{n}_p}{\omega - \epsilon_p + i\eta}\right), \qquad (6)$$

where ϵ_p are HF orbital energies and $n_p = 1 - \bar{n}_p$ denote the usual occupation numbers in the HF ground state. As for $G(\omega)$, there is a direct perturbation expansion for $\Sigma(\omega)$ which can be formulated in terms of the famous Feynman diagrams. The self-energy can be written as the sum

$$\Sigma(\omega) = \Sigma(\infty) + M(\omega) \qquad (7)$$

of a static part $\Sigma(\infty)$ and a dynamic (ω-dependent) part $M(\omega)$. The latter has a spectral resolution[40,41]

$$M_{pq}(\omega) = \sum_\mu \frac{m_p^{(\mu)} m_q^{(\mu)*}}{\omega - \omega_\mu + i\eta\sigma_\mu} \qquad (8)$$

similar to $G(\omega)$, where $\sigma_\mu = \pm 1$. Corresponding to the sign of σ_μ, the poles of $M(\omega)$ lie in the upper and lower complex ω plane, respectively, and thus $M(\omega)$ can be written as the sum

$$M(\omega) = M^-(\omega) + M^+(\omega) \qquad (9)$$

of two parts $M^-(\omega)$ and $M^+(\omega)$ associated with states of the $(N-1)$- and $(N+1)$-particle systems; respectively. As has been shown in Ref. 36, the diagrammatic perturbation expansion for $M(\omega)$ can correspondingly be decomposed into two separate expansions for $M^-(\omega)$ and $M^+(\omega)$.

The starting point of the ADC scheme is the observation that both parts $M^\pm(\omega)$ can be represented in the algebraic form

$$M_{pq}(\omega) = U_p^\dagger(\omega 1 - K - C)^{-1}U_q \qquad (10)$$

which may be viewed as a generalization of the special (diagonal) form of the spectral representation (8). Here, and in the following, the superscripts $\pm$ are dropped if not essential. The quantities introduced by Eq. (10) are a constant Hermitean matrix G referred to as the effective interaction matrix, a diagonal matrix K of zeroth-order (HF) ionization energies, and columns U_p of effective coupling matrix elements for the one-particle orbitals p. The configuration space defining these quantities in the case of $M^-(\omega)$ is spanned by the unperturbed (HF) states $|\Phi_J^{N-1}\rangle$ of the $(N-1)$-particle system with the exception of the single hole (1h) states. In the usual classification these states are denoted as two-hole–one-particle (2h–1p) states, 3h–2p states, etc. The corresponding space in the case of $M^+(\omega)$ is spanned by the 2p–1h, 3p–2h,..., states of $N+1$ particles.

The effective quantities U_p and C have perturbation expansions

$$U_p = U_p^{(1)} + U_p^{(2)} + U_p^{(3)} + \cdots, \qquad (11a)$$

$$C = C^{(1)} + C^{(2)} + C^{(3)} + \cdots \qquad (11b)$$

beginning in first order. Inserting these expansions in the ADC form (10) one can generate a perturbation expansion of the latter. Comparing the perturbation expansion of the ADC form with the original diagrammatic expansions of $M^-(\omega)$ or $M^+(\omega)$ through a given order n of perturbation theory, one may determine successively the individual contributions in the expansions (11) of U_p and C. In general, one obtains, for a given order n, finite expansions $U_p(n)$ and $C(n)$ that define, together with the ADC form (10), a systematic [ADC(n)] approximation for $M^\pm(\omega)$. According to their construction, the ADC(n) approximations sum the perturbation expansions of $M^\pm(\omega)$ completely through order n and partially through infinite order. An essential property of these approximations is that the explicit configuration spaces required grow relatively slowly with increasing order n: for $n = 2$ and 3 the configuration space is confined to the 2h–1p (M^-) and 2p–1h (M^+) states, and in each even order $n = 2m$ the configuration space has to be enlarged by the next higher class of $(m+1)$h–mp and $(m+1)$p–mh states, respectively.

Once the matrix C and the columns U_p have been determined, the spectral energies ω_μ of $M^\pm(\omega)$ may be derived from the respective eigenvalue problems

$$(K + C)Y = Y\Omega, \quad Y^\dagger Y = 1, \qquad (12)$$

where Ω is the diagonal matrix of eigenvalues ω_μ and Y is the matrix of eigenvectors. The amplitudes $m_p^{(\mu)}$ of the self-energy part [see Eq. (8)] then are obtained according to

$$m_p^{(\mu)} = U_p^\dagger Y^{(\mu)} \qquad (13)$$

as the (scalar) product of U_p and the μth eigenvector $Y^{(\mu)}$. The Dyson equation (5) can now be cast into the following eigenvalue problem:

$$AX = XE, \quad X^\dagger X = 1,$$

$$A = \begin{pmatrix} \epsilon + \Sigma(\infty) & m^+ & m^- \\ (m^+)^\dagger & \Omega^+ & 0 \\ (m^-)^\dagger & 0 & \Omega^- \end{pmatrix}, \qquad (14)$$

where ϵ denotes the diagonal matrix of HF orbital energies, $\Omega^\pm$ are the diagonal matrices of the spectral energies ω_μ [Eq. (12)] for the self-energy parts $M^\pm(\omega)$, and $m^\pm$ are the corresponding matrices of coupling amplitudes $m_p^{(\mu)\pm}$. The one-particle Green's function is obtained according to

$$G_{pq}(\omega) = \sum_m \frac{x_p^{(m)} x_q^{(m)*}}{\omega - e_m} \qquad (15)$$

from the eigenvalues $e_m = E_{mm}$ and the eigenvector components $x_p^{(m)} = X_{pm}$ of the matrix A. Numerical strategies for calculating the Green's function according to this "two-step-diagonalization" procedure have been discussed by von Niessen et al.[31] Alternatively, the eigenvalue problem (14) of the Dyson equation and the preceding diagonalizations of the ADC matrices $(K + C)^\pm$ according to Eqs. (12) and (13) can be unified to the following eigenvalue problem:

$$BX = XE, \quad X^\dagger X = 1,$$

$$B = \begin{pmatrix} \epsilon + \Sigma(\infty) & (U^+)^\dagger & (U^-)^\dagger \\ U^+ & (K + C)^+ & 0 \\ U^- & 0 & (K + C)^- \end{pmatrix}. \qquad (16)$$

The one-particle Green's function is again obtained in the form of Eq. (15). This one-step diagonalization procedure is especially useful, if the matrices $(\mathbf{K}+\mathbf{C})^{\pm}$ are large. One may then resort to a Davidson diagonalization method[42] to determine selected eigenvalues and eigenvectors of $\mathbf{B}$. As another possibility one may employ the Lanczos method[43] to generate the desired information from $\mathbf{B}$.

C. The static self-energy part

In the following we consider the static self-energy part $\Sigma(\infty)$ which enters the 1h/1p block of the secular matrices $\mathbf{A}$ and $\mathbf{B}$ in Eqs. (14) and (15), respectively. An obvious approach to $\Sigma(\infty)$ is to evaluate its direct diagrammatic perturbation expansion through a finite order n, which presently is feasible through fourth order.[44] The direct perturbation series, however, has often only a slow and oscillating convergence, and therefore the use of a third- or fourth-order expansion of $\Sigma(\infty)$ may cause a relatively large error in the results for the single hole main states (see the discussion in Sec. V). A more consistent approximation follows from the observation that $\Sigma(\infty)$ is determined by the dynamic self-energy part $\mathbf{M}(\omega)$ through the well-known relation[28,40,41]

$$\Sigma_{pq}(\infty) = \sum_{k,l} V_{pk[ql]} \frac{1}{2\pi i} \oint [G_{lk}(\omega) - G_{lk}^0] d\omega. \quad (17)$$

Here, $V_{ij[kl]} = V_{ijkl} - V_{ijlk}$ denotes the antisymmetrized Coulomb integral; the contour integration closes in the upper complex ω plane, i.e., encloses all $(N-1)$-particle poles. Together with the Dyson equation (5) and Eqs. (6) and (7), Eq. (17) represents an implicit equation for $\Sigma(\infty)$ once $\mathbf{M}(\omega)$ [or an approximation to $\mathbf{M}(\omega)$] is given. The iterative solution of this implicit equation, discussed in Ref. 31, requires at each iteration step to determine the amplitudes $x_p^{(n)}$ for all $(N-1)$-particle states $|\Psi_n^{N-1}\rangle$ from the secular problem (15) or (16), respectively, and is thus numerically very expensive. Fortunately, an excellent explicit approximation to the fully iterated result of Eq. (17) may be obtained by replacing the integrand on the right-hand side by the first term of the Dyson expansion

$$\mathbf{G} - \mathbf{G}^0 = \mathbf{G}^0[\Sigma(\infty) + \mathbf{M}(\omega)]\mathbf{G}^0 + \cdots. \quad (18)$$

Thereby, Eq. (17) becomes

$$\Sigma_{pq}(\infty) = \sum_{k,l} V_{pk[ql]} \frac{1}{2\pi i} \oint d\omega\, G_{ll}^0(\omega) [\Sigma_{lk}(\infty)$$
$$+ M_{lk}(\omega)] G_{kk}^0(\omega) \quad (19)$$

which after performing the contour integration represents a set of linear inhomogeneous equations for the matrix elements of $\Sigma(\infty)$. The error introduced by truncating the Dyson expansion according to Eq. (18) is of fifth order since $\mathbf{M}(\omega)$ and $\Sigma(\infty)$ begin in second and third order, respectively, if the usual ground state HF representation is assumed.

In Ref. 31 explicit expressions for the Eqs. (19) have been given and discussed. According to this formulation the evaluation of the inhomogeneity [associated with the contour integration over $\mathbf{G}^0(\omega)\mathbf{M}(\omega)\mathbf{G}^0(\omega)$] requires the explicit diagonal representation of $\mathbf{M}(\omega)$, i.e., the full diagona-

lization of both ADC matrices $(\mathbf{K}+\mathbf{C})^{\pm}$. Clearly, this represents a major numerical obstacle, preventing in particular the one-step diagonalization approach to the secular equation (16) intended here. In the course of this work a better approach was found, allowing to determine the inhomogeneity directly and efficiently from the matrices $(\mathbf{K}+\mathbf{C})^{\pm}$. A report on this new technique will be given elsewhere.[44]

D. Explicit ADC equations

The derivation and analysis of the explicit ADC(n) schemes for $n = 2, 3$, and 4 has been given previously.[36] Here we may confine ourselves to a description of their structure and a brief account of essential properties.

The ADC(2) scheme recovers just the simple second-order approximation to $\mathbf{M}(\omega)$. Here, the effective coupling matrix elements are of first order:

$$U_{p,jkl} = U_{p,jkl}^{(1)} = V_{pj[kl]} \quad (20)$$

and the effective interaction matrix $\mathbf{C}$ vanishes. The explicit configuration spaces for $\mathbf{M}^{\pm}(\omega)$ are spanned by the 2h–1p states further specified by the triple (j,k,l) of one-particle quantum numbers with $\bar{n}_j n_k n_l = 1 (k < l)$ and by the 2p–1h states (j,k,l) with $n_j \bar{n}_k \bar{n}_l = 1 (k < l)$, respectively. These configuration spaces are maintained in the ADC(3) scheme. Here the matrix elements of $\mathbf{U}$ are needed through second order:

$$U_{p,jkl} = U_{p,jkl}^{(1)} + U_{p,jkl}^{(2)} \quad (21a)$$

while the first-order expansion

$$C_{jkl,j'k'l'} = C_{jkl,j'k'l'}^{(1)} \quad (21b)$$

is employed for the effective interaction $\mathbf{C}$. The ADC(3) equations together with a consistent static self-energy part (see Sec. II B) have also been referred to as the extended 2ph-Tamm–Dancoff approximation (2ph-TDA). Essentially equivalent third-order schemes were derived previously within the equation-of-motion approach (EOM) and the related superoperator/inner-projection representation of the electron propagator.[29,30,46] On this level of approximation the energies and spectroscopic amplitudes of single hole (particle) main states are treated consistently through third order of perturbation theory, while a first- and second-order description, respectively, is achieved for the class of 2h–1p (2p–1h) satellite states.

In the fourth-order scheme [ADC(4)] the next higher class of satellite states, namely 3h–2p (3p–2h) states comes explicitly into play. The expansions of the matrix elements already present in the ADC(3) scheme grow by one order, i.e.,

$$U_{p,jkl} = U_{p,jkl}^{(1)} + U_{p,jkl}^{(2)} + U_{p,jkl}^{(3)}, \quad (22a)$$

$$C_{jkl,j'k'l'} = C_{jkl,j'k'l'}^{(1)} + C_{jkl,j'k'l'}^{(2)}. \quad (22b)$$

The new contributions are
(i) effective coupling matrix elements for the 3h–2p (3p–2h) states in second order:

$$U_{p,ijklm} = U_{p,ijklm}^{(2)} \quad (22c)$$

where the quintuples (i,j,k,l,m) refer to 3h–2p states with $\bar{n}_i \bar{n}_j n_k n_l n_m = 1$ (or 3p–2h states with $n_i n_j \bar{n}_k \bar{n}_l \bar{n}_m = 1$);

(ii) first-order effective interaction matrix elements

$$C_{jkl,i'j'k'l'm'} = C^{(1)}_{jkl,i'j'k'l'm'} \qquad (22d)$$

for the 2h–1p and 3h–2p (2p–1h and 3p–2h) states; and

(iii) first-order matrix elements

$$C_{ijklm,i'j'k'l'm'} = C^{(1)}_{ijklm,i'j'k'l'm'} \qquad (22e)$$

for the 3h–2p (3p–2h) states. The explicit expressions for the matrix elements (21) and (22) of the third- and fourth-order ADC scheme, respectively, have been specified in Ref. 36.

Together with the secular equation (16) and the consistent treatment of the static part $\Sigma(\infty)$ according to Sec. II C, these equations constitute the full ADC(4) scheme for the one-particle Green's function $G(\omega)$. Its results for the ionization energies and spectroscopic amplitudes of the single hole (particle) main states are consistent through fourth order. In the conventional wave function approach this level of description requires configuration interaction (CI) expansions for the (initial) ground state and for the ionic states including single through quadruple excitations on the HF ground state and HF single-hole states, respectively. By contrast, the ADC(4) scheme consists in a single secular equation requiring an explicit configuration space of single and double excitations on the single-hole and single-particle HF states. Here the effect of ground state correlation and of the ionic triple and quadruple excitations are implicitly taken into account by means of the higher order terms in the effective quantities U and C and by the coupling of $(N-1)$- and $(N+1)$-particle contributions in the final secular (Dyson) equation (14) or (16). A distinctive improvement with respect to the third-order [ADC(3)] scheme is achieved for the class of 2h–1p (2p–1h) satellite states. Their ionization energies (and spectroscopic factors) are calculated consistently through second (third) order, which means that both ground state correlation and the mixing with 4h–3p (4p–3h) states are taken into account. Finally, the next higher class of satellite states, i.e., 3h–2p (3p–2h) states are treated explicitly in the ADC(4) scheme yielding first- and second-order consistency for the energies and spectroscopic amplitudes, respectively.

The ADC equations reflect the symmetry properties of the respective systems (Hamiltonians), i.e., they decouple with respect to the irreducible representations of the underlying symmetry group. This means that, in particular, spin-free equations for the ionic doublet (or higher multiplet) states can be formulated from the general expressions in Ref. 36. In the case of the third-order scheme [ADC(3)], the details and the resulting working equations have been described previously.[47] The treatment of the ADC(4) equations is analogous, though somewhat more cumbersome. Here, one has to deal with the 32-fold degeneracy of 3h–2p (3p–2h) states and with 23 distinct quadruple summations contributing to $U^{(3)}_{p,jkl}$. A spin-free version of the full ADC(4) equations has been formulated and coded, partly with the aid of a special computer program[45] performing the formal transformations between the primitive (spin–orbital) and spin-adapted (doublet) configurations.

Though more economical than comparable CI expansions the full ADC(4) equations are very costly and their application poses formidable computational problems. An obvious bottleneck is the size of the required configuration space, in particular, of the 3h–2p and 3p–2h spaces. Another bottleneck is the calculation of the third-order effective coupling matrix elements $U^{(3)}_{p,jkl}$ involving quadruple summation over one-particle quantum numbers. The calculations performed so far concerned small systems like H_2, He, and Be or larger systems (N_2, H_2O) using very restricted basis sets.[45] It should be noted that partial inclusion of fourth-order terms was considered by Baker in several applications.[35,48] For the application to K-shell ionization intended here a substantial reduction of the ADC(4) equation results if the correlation between K-shell (core) and valence electrons is neglected. This approximation is briefly discussed in Sec. II E.

E. Core–valence separation

The K-shell and valence levels of a molecule like N_2 or CO are energetically well separated, and the neglect of core–valence correlation introduces only a relatively small error, e.g., about 1–2 eV in the case of N_2 ground state energy. Moreover, for the direct calculation of energy differences such as ionization or excitation energies there is an effective cancellation of the core–valence correlation effects in the initial and final states and their neglect provides a very efficient and good approximation.

Formally, this core–valence separation approximation to the ADC(4) equations results from neglecting the following types of Coulomb integrals[49]:

$$V_{cijk} = V_{icjk} = \cdots = 0,$$
$$V_{cc'c''j} = V_{cc'jc''} = \cdots 0, \qquad (23)$$
$$V_{cc'ij} = V_{ijcc'} = 0,$$

where c, c', and c'' label core orbitals and i,j,k refer to occupied valence or unoccupied (virtual) orbitals. Apart from cancellations the error introduced herewith into the ionization energies is of the order $V^2/\Delta\epsilon$, where V stands for a neglected Coulomb integral and $\Delta\epsilon$ is the core–valence energy separation. As a consequence of this approximation the secular equation (16) decouples into several subproblems; in particular, the K-shell hole states are obtained from the secular matrix

$$\mathbf{B}^c = \begin{pmatrix} \epsilon + \Sigma(\infty) & (\mathbf{U}^-)^\dagger \\ \mathbf{U}^- & (\mathbf{K} + \mathbf{C})^- \end{pmatrix}, \qquad (24)$$

defined entirely in the space of cationic $(N-1)$ states comprising the single core hole states and all 2h–1p and 3h–2p states with one (and only one) core hole. Obviously, this means a substantial reduction of the full secular problem, being now of the size of the usual single determinant double excitation CI problem. Besides the reduction of the configuration space, also the effective quantities $\mathbf{U}^-$ and $\mathbf{C}^-$ in $\mathbf{B}^c$ simplify considerably as many terms of the full expressions in Ref. 36 vanish upon the neglect of the Coulomb integrals (23).

Unfortunately, one does not completely get rid of the valence part by the core–valence separation approximation, since this part enters the calculation of the static self-energy matrix elements $\Sigma_{cc'}(\infty)$ required in $\mathbf{B}_c$. The relation (17)

specialized to core orbitals c,c' and in the core–valence separation approximation reads

$$\Sigma_{cc'}(\infty) = \sum_{k,l \notin \text{core}} V_{ck[c'l]} \frac{1}{2\pi i}$$

$$\times \oint [G_{lk}(\omega) - G_{lk}^{0}(\omega)] d\omega, \qquad (25)$$

where the summation over k and l runs over occupied valence and virtual orbitals only. The evaluation of these matrix elements as described in Sec. II C requires to deal with the valence parts of $(\mathbf{K} + \mathbf{C})^{\pm}$ and $\mathbf{U}^{\pm}$.

The ionization energies and spectroscopic factors of the core hole states are obtained as the eigenvalues and eigenvector components of $\mathbf{B}^c$ as described in Sec. II B. We note in passing the sum rule

$$\sum_{n} e_n x_c^{(n)} x_{c'}^{(n)*} = \epsilon_c \delta_{cc'} + \Sigma_{cc'}(\infty) \qquad (26)$$

for the core hole states according to the eigenvalue problem of $\mathbf{B}^c$.

III. CALCULATIONS

The orbital energies and Coulomb integrals of a HF calculation for the ground state of the neutral molecule are required as the input data for the ensuing Green's function calculations. The HF calculations for N_2 and CO at the equilibrium nuclear geometries (2.069 a.u. for N_2 and 2.132 a.u. for CO) were performed in the usual LCAO-SCF procedure employing the ATMOL program package.[50] The basis set of atomic orbitals was the $5s/4p/1d$ contraction of $11s/7p/1d$ Cartesian Gaussians, where the exponents and contraction coefficients for the s and p functions were taken from the work of Salez and Veillard[51] (contraction Nos. 14, 10, and 13 for s orbitals in N, C, and O, respectively, contraction No. 8 for p orbitals). The exponents for the d functions are 0.6, 0.75, and 0.8 for C, N, and O, respectively. The number of the resulting molecular orbitals (MOs) is 46, and the resulting total energies are -108.9750 and -112.7671 a.u. for N_2 and CO, respectively.

For the present ADC(4) calculations of molecular K-shell ionization spectra a special version of the previous general ADC(4) code was developed invoking the core–valence separation approximation and introducing improved numerical procedures. While the spin symmetry was used from the outset to reduce the size of the secular problem, the spatial symmetry was exploited only to the extent of the respective largest Abelian subgroup, e.g., D_{2h} and C_{2v} in the case of N_2 and CO, respectively. Then the irreducible representations are one dimensional and the problem of constructing symmetry-adapted configurations is trivial. In the present calculations the secular dimension was 12 945 each for the N1s, C1s, and O1s hole states of $^2A_{1(g)}$ symmetry.

The static self-energy part $\Sigma(\infty)$ was determined by the direct approach described in Sec. II C and in Refs. 31 and 44 on the level of the ADC(3) approximation for $\mathbf{C}$ and $\mathbf{U}$. As has been mentioned, this yields a complete fourth-order treatment of $\Sigma(\infty)$ and may legitimately be used in the present fourth-order scheme.

A new efficient block Davidson routine has been employed to calculate the lowest roots and eigenvectors of the secular matrix.[52] A characteristic CPU time for eight roots and a matrix size as specified above was 750 s on an IBM 3090. The buildup of the secular matrix here took 670 s. The calculated ionization energies are vertical energies and are to be compared with the centroids of the experimental peaks. Relativistic corrections of 0.1, 0.2, and 0.4 eV for C1s, N1s, and O1s states according to the work of Pekeris[53] should be taken into account when comparing the present result with experiment.

IV. RESULTS AND DISCUSSION
A. N_2

The ground state of the N_2 molecule has the electron configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2 \ ^1\Sigma_g^+.$$

There are two almost degenerate core orbitals $1\sigma_g$ and $1\sigma_u$ associated with the symmetric and antisymmetric linear combination of the atomic $1s$ orbitals, respectively. Corresponding to the possibility of creating a hole in the $1\sigma_g$ or $1\sigma_u$ orbital, the core hole states of N_2 occur in pairs of nearly degenerate states of g and u symmetry. Their energy splitting is in the order of the difference of the orbital energies $\epsilon_{1\sigma_g} = -426.95$ eV and $\epsilon_{1\sigma_u} = -426.85$ eV. In the following we shall consider only the class of g states.

The ionization energies and spectroscopic factors (relative intensities) of the lowest $^2\Sigma_g^+$ $1s$ hole states obtained by the ADC(4) Green's function calculation are given in Table I together with experimental values and previous theoretical results. For the $(1\sigma_g)^{-1}$ single hole (main) state an ionization energy of 410.0 eV has been calculated. Taking into account an estimated relativistic correction of $+0.2$ eV and compensating for the effect of the core–valence separation approximation by a correction of -0.4 eV (see Sec. V) one arrives at a relativistically corrected full ADC(4) result of 409.8 eV, which is in excellent agreement with the experimental ionization energy. This level of accuracy for absolute ionization energies has previously been reached only by the large-scale CI calculations of Butscher et al.[21]

The spectroscopic factor of the $(1\sigma_g)^{-1}$ main state has been calculated as 0.66, which means that 34% of the N1s photoionization cross section appears in shakeup (and shake-off) satellites on the high binding energy side of the main peak. The first and second shakeup feature arising in the K-shell photoelectron spectrum of N_2 are due to excitations of an electron from the occupied $1\pi_u$ orbital to the unoccupied $1\pi_g$ (π^*) orbital. The electron configuration $(1\sigma_u)^{-1}(1\pi_u)^{-1}(1\pi_g)^1$ gives rise to two distinct $^2\Sigma_g^+$ states differing with respect to the spin coupling of the π electrons: an intermediate π–π^* triplet ($S' = 1$) and a singlet ($S' = 0$) state correspond to the first and second satellite peak, respectively. This assignment and characterization, which was clarified by Rodwell et al.[19] and subsequent studies by Butscher et al.[21] and Ågren et al.,[22] is confirmed by the present results. The analysis of the ADC(4) eigenvectors shows for the first state about 80% π–π^* character and an almost pure intermediate triplet representation. In accor-

TABLE I. Vertical ionization energies and relative intensities (spectroscopic factors) of $^2\Sigma_g^+$ states in the N1s photoelectron spectrum of N_2.

Main configuration		Ionization energies (eV)[a]					Relative intensities			
		ADC(4)[b]	CI[c]	CI[d]	CI[e]	Expt.[f]	Expt.[f]	CI[c]	CI[e]	ADC(4)[b]
	$1\sigma_g^{-1}$	410.00	⋯	410.01	408.4	409.9	100	100	100	100(0.66)[g]
$1\sigma_u^{-1}$	$1\pi_u^{-1}1\pi_g^1(S'=1)$	+9.32	9.55	9.39	9.67	9.3	2.1	1.2	1.2	1.9
	$1\pi_u^{-1}1\pi_g^1(S'=0)$	17.59	16.82	⋯	18.21	16.6	8.0[h]	7.9	7.0	8.8
$1\sigma_{g/u}^{-1}$	$3\sigma_g^{-1}4\sigma_g^1/3\sigma_u^1$	21.70			25.37				0.5	0.001
	$3\sigma_g^{-1}3\sigma_u^1$	22.46			26.42				0.3	0.03
	$3\sigma_g^{-1}4\sigma_g^1/3\sigma_u^1$	22.74								0.03
	$3\sigma_g^{-1}4\sigma_g$	23.51								0.06
	$1\pi_u^{-1}2\pi_u^1 + 3\sigma_g^{-1}5\sigma_g^1$	24.12								0.1
	$1\pi_u^{-1}2\pi_u^1 + 3\sigma_g^{-1}5\sigma_g^1$	24.53								0.05
	$1\pi_u^{-2}1\pi_g^2$	25.28	19.74		20.64			0.2	2.8	0.1
	$1\pi_u^{-2}1\pi_g^2 + 3\sigma_g^{-1}5\sigma_g^1$	25.64								0.35

[a] Estimated relativistic correction (to be added to the theoretical energies) is 0.2 eV.
[b] Present results.
[c] Rodwell et al. (Ref. 19).
[d] Butscher et al. (Ref. 21).
[e] Ågren et al. (Ref. 22).
[f] Gelius (Ref. 2).
[g] Absolute value of spectroscopic factor in brackets.
[h] Result by Gelius quoted in Ref. 22.

dance with observations by Rodwell et al.,[19] the second state has already appreciable admixtures of π–π^* double excitations (3h–2p states); its π–π^* single excitation contributions representing the intermediate singlet ($S'=0$) amount to only 50% of the total weight. While the calculated shakeup (excitation) energy of the first (triplet) satellite is in very good accord with experiment, the present result for the second state is too high by 1.0 eV as a consequence of the admixture of 3h–2p states treated with lower accuracy in the ADC(4) scheme. The relative intensities of the two π–π^* satellites are well reproduced by the present calculations. It should be noted that within the usual CI treatment based on different SCF calculations for the states of the neutral molecule and the cation, the evaluation of the spectroscopic factors $|x_{1\sigma_g}^{(n)}|^2 = |\langle \Psi_n^{N-1}|c_{1\sigma_g}|\Psi_0^N\rangle|^2$ [Eq. (4)] represents a formidable problem. The relative intensities reported by Rodwell et al.[19] and by Ågren et al.[22] (see Table I) are obtained from very limited CI expansions and are far less reliable than their large CI results for the energies.

The large energy gap between the two π–π^* satellite states as well as their different intensities are properties that can be explained already on the level of an appropriate zeroth-order representation of the respective wave functions. A detailed discussion including explicit expressions for the zeroth-order satellite states and first-order energy matrix elements has been presented elsewhere.[54] The essential point of this analysis is that the first-order energy separation of the two satellite states $|S'\rangle$ with the intermediate spin of the valence electrons being $S' = 0$ and 1, respectively, is essentially given by the contribution

$$\langle 0|\hat{H}|0\rangle - \langle 1|\hat{H}|1\rangle \sim 2\cdot(K_{\pi_x^*,\pi_x} + V_{\pi_x^*,\pi_y,\pi_x,\pi_y^*})$$

of rather large valence exchange integrals. In the framework of a small SCF calculation employing Dunning's[55] 3s/2p contracted basis this energy separation amounts to 13.6 eV. The coupling matrix element between the two zeroth-order satellite states

$$\langle 0|\hat{H}|1\rangle = \frac{\sqrt{3}}{2}(-K_{\sigma,\pi} + K_{\sigma,\pi^*}),$$

on the other hand, contains only small core–valence exchange integrals, which, moreover, partly cancel each other; here a value of 0.01 eV was calculated. These first-order properties make clear that, indeed, the spin-coupling scheme chosen here is a good representation of actual satellite states and explain their energy separation. The spectroscopic amplitudes of these states in first order read

$$x_{1\sigma_g}^{(0)} = (\Delta\epsilon)^{-1}(2V_{1\sigma_g,\pi_x^*,1\sigma_u,\pi_x} - V_{1\sigma_g,\pi_x^*,\pi_x,1\sigma_u}),$$

$$x_{1\sigma_g}^{(1)} = -(\Delta\epsilon)^{-1}\sqrt{3}\,V_{1\sigma_g,\pi_x^*,\pi_x,1\sigma_u},$$

where $\Delta\epsilon = \epsilon_{\pi^*} - \epsilon_\pi$. Inserting here the integrals of the small SCF calculation these amplitudes are -0.6 and 12.5 eV/$\Delta\epsilon$ for the first ($S'=1$) and second ($S'=0$) satellite state, respectively. That is, there is a very large coupling of the singlet ($S'=0$) satellite to the $1\sigma_g$ hole state, mediated by the direct coupling integral $V_{1\sigma_g,\pi_x^*,1\sigma_u,\pi_x}$, whereas the triplet ($S'=1$) satellite couples in first order only by the small exchange integral $V_{1\sigma_g,\pi_x^*,\pi_x,1\sigma_u}$. According to these first-order results, the large spectroscopic factor (relative intensity) of the singlet satellite seems not to be an effect of ground state correlation as has been claimed by Rodwell et al.[19] and by Ågren et al.[22]

At higher shakeup energy the assignment of spectral

peaks is no longer clear. Our calculation predicts valence–Rydberg excitations of the type $3\sigma_g-n\sigma_g$ and $3\sigma_g-n\sigma_u$ beginning at 21.7 eV, and a series of $1\pi_u-n\pi_u/n\pi_g$ excitations above 24 eV. However, the calculated relative intensities are rather small (below 0.2%) and it might be difficult to observe these Rydberg-type satellites in the experimental spectrum. The Rydberg series are perturbed by $\pi-\pi^*$ double excitations, the first of which is placed at 25 eV by our calculation. This energy is certainly too high by several eV, a consequence of incompletely treated relaxation for this class of states. In accord with the previous (relaxed) CI results by Rodwell et al.[19] and Ågren et al.,[22] the first doubly excitations are expected at about 20 eV (vertical) shakeup energy. However, it is doubtful whether these doubly excited satellites are directly visible in the experimental spectrum, since the promotion of two bonding π electrons into the nonbonding π^* orbital is expected to be accompanied by an extraordinary vibrational broadening. It seems that none of the relatively narrow experimental peaks at 19.6, 23.0, and 24.6 can be correlated to a $\pi-\pi^*$ double excitation. Of course, the presence of low lying $\pi-\pi^*$ double excitations may become apparent by perturbations of the energy positions and intensity distributions of the Rydberg-type satellites. An adequate theoretical description here requires, besides a better treatment of the 3h–2p states in the static calculations, dynamical calculations allowing for multistate vibronic interaction (see Cederbaum and Köppel[56]).

The lowest N1s satellite states of symmetry other than $^2\Sigma_g^+$ are compiled in Table II. According to the monopole selection rules of direct shakeup these states are not expected to appear in the photoelectron spectrum. However, they may obtain intensity due to the conjugate shakeup mechanism[57] or due to the effect of ground state correlation. In the case of the lowest $^2\Pi_u$ state, $[(1\sigma_u)^{-1}(3\sigma_g)^{-1}(1\pi_g)^1]$, e.g., the conjugate contribution to the intensity amplitude is essentially given by the product $\langle 1\sigma_u|\hat{t}|1\pi_g\rangle\langle 3\sigma_g|\epsilon_{\sigma_g}\rangle$ of the $1s-\pi^*$ dipole matrix element and the overlap integral between the $3\sigma_g$ and the σ_g continuum orbital.[54] The dipole matrix element corresponding to the N1s–$1\pi_g$ core–valence excitation is known to be rather large so that the conjugate contribution could play a role if the overlap integral is not too small, possibly in the case of low kinetic energy of the continuum electron.

TABLE II. N1s hole states of $^2\Pi_g$, $^2\Delta_g$, and $^2\Sigma_g^-$ symmetry.

Symmetry	Main configuration		$I_n - I_{1\sigma_g}$ (eV)
$^2\Pi_g$	$1\sigma_g^{-1}$	$3\sigma_g^{-1}\pi_g^1$	8.46
$^2\Pi_g$		$3\sigma_g^{-1}1\pi_g^1$	10.01
$^2\Delta_g$	$1\sigma_u^{-1}$	$1\pi_u^{-1}1\pi_g^1$	10.40
$^2\Sigma_g^-$		$1\pi_u^{-1}1\pi_g^1$	10.44
$^2\Delta_g$		$1\pi_u^{-1}1\pi_g^1$	11.14
$^2\Sigma_g^-$		$1\pi_u^{-1}1\pi_g^1$	11.57
$^2\Pi_g$	$1\sigma_u^{-1}$	$2\sigma_u^{-1}1\pi_g^1$	13.43
$^2\Pi_g$		$2\sigma_u^{-1}1\pi_g^1$	15.05
$^2\Pi_g$		$3\sigma_g^{-1}2\pi_u^1$	22.09
$^2\Pi_g$		$3\sigma_g^{-1}2\pi_u^1$	22.25
$^2\Pi_g$		$3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2$	22.89

It is interesting to note that the lowest N1s shakeup state is a $^2\Pi_g$ (or $^2\Pi_u$) state arising from the $3\sigma_g-\pi^*$ excitation. This state, characterized as the intermediate valence triplet is placed about 1 eV below the first $^2\Sigma_g^+$ satellite. The corresponding singlet state is found 1.5 eV above the former state, i.e., the separation energy is considerably smaller than in the case of the two $^2\Sigma_g^+$ ($\pi-\pi^*$) satellites. A similar pair of $^2\Pi_g$ states is found for the excitation $2\sigma_u-\pi^*$ at 13.4 and 15.0 eV, while the next two states correspond already to a valence–Rydberg excitation $(3\sigma_g-2\pi_u)$. The energy splitting of the latter states is only 0.16 eV owing to the small $3\sigma_g-2\pi_u$-exchange integral; these states are no longer adequately represented by the spin-coupling scheme employed for the valence excitations.

In addition to the $^2\Sigma_g^+$ satellites already discussed, the satellite configuration $(1\sigma_u)^{-1}(1\pi_u)^{-1}(1\pi_g)^1$ gives rise to a manifold of each two states of $^2\Sigma_g^-$ and $^2\Delta_g$ symmetry. These states are situated in a relatively small interval between the $^2\Sigma_g^+$ triplet and singlet state. The exchange splittings of these states are quite small and they do fit much less in the above valence coupling scheme. The last state listed in Table II is the first double excitation of $^2\Pi_g$ symmetry. According to what has been stated above, the calculated excitation energy of 22.9 eV is certainly too large by 3–5 eV.

B. CO

The ground state electron configuration of CO is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2 {}^1\Sigma^+.$$

Here 1σ and 2σ denote the atomic O1s and C1s orbitals, respectively, which are energetically well separated: on the level of the present SCF calculation the orbital energies are $\epsilon_{1\sigma} = -562.43$ eV and $\epsilon_{2\sigma} = -309.29$ eV. While the C1s spectrum, at least its low energy region, is similar to the N1s spectrum of N_2, the O1s spectrum shows a strikingly different structure.

1. C1s

Table III collects the present and previous theoretical results[20] of the C1s hole states together with recent experimental data.[9] The theoretical C1s binding energy given here may be corrected for relativistic effects ($+ 0.1$ eV) and for the effect of the core–valence separation approximation ($- 0.4$ eV). The resulting value of 296.7 eV is 0.5 eV below the experimental result. It should be noted that a somewhat smaller experimental value (296.0 eV) has been concluded by Petterson et al.[58] recently from C1s x-ray emission measurements. No theoretical calculation beyond the ΔSCF level is available for comparison.

As in N_2 the first two shakeup features correspond to $\pi-\pi^*$ ($1\pi-2\pi$) valence excitations of symmetry $^2\Sigma^+$ differing with respect to the intermediate spin $S' = 1$ and 0 of the electrons in the open π shells. The excitation energies of our ADC(4) calculation lie 0.8 and 2.2 eV above the experimental energies for the triplet and singlet satellite, respectively. Again, the large discrepancy for the second satellite is an indication for strong admixtures of 3h–2p states, mainly $\pi-\pi^*$ double excitations, for which the present method fails to

TABLE III. Vertical ionization energies and relative intensities (spectroscopic factors) of $^2\Sigma^+$ states in the C1s photoelectron spectrum of CO.

Main configuration Expt.[d] ADC(4)[b]	Ionization energies (eV)[a] ADC(4)[b] Expt.[d]			Relative intensities CI[c] CI[c]		
$2\sigma^{-1}$	296.08	...	296.2	100	100	100(0.68)[e]
$2\sigma^{-1}1\pi^{-1}2\pi^1(S'=1)$	+9.11	8.54	8.3	2.3	1.4	2.2
$1\pi^{-1}2\pi^1(S'=0)$	17.12	15.71	14.9	4.8	3.5	5.0
$5\sigma^{-1}6\sigma^1$	19.89		17.9	1.9		1.3
$1\pi^{-2}2\pi^2$	20.79	18.26	...	...	2.1	0.4
$5\sigma^{-1}6\sigma^1$	21.18		19.2	1.1		0.2
$5\sigma^{-1}7\sigma^{-1}$	21.64		20.1	1.6		1.7
$1\pi^{-2}2\pi^2 + 5\sigma^{-1}7\sigma$	22.31	...	...			0.7

[a] Estimated relativistic correction (to be added to the theoretical energies) is 0.1 eV.
[b] Present results.
[c] Guest et al. (Ref. 20).
[d] Svensson et al. in Ref. 9.
[e] Absolute value of spectroscopic factor in brackets.

generate the proper relaxation shifts. Their influence on the results is still larger than in the case of N_2, as they appear here at distinctly lower excitation energy. We note that also the CI results by Guest et al.,[20] though in better accord with the experimental energies, show this tendency to overshoot.

About 3 eV above the singlet π–π^* satellite other states appear, the assignment of which is less clear. Our calculation predicts a pair of 5σ–6σ valence–Rydberg excitations at 19.9 and 21.2 eV vertical shakeup energy, respectively. Since both the 5σ and the $n\sigma$ Rydberg orbitals are nonbonding the effect of vibrational broadening should only be small here, and narrow spectral peaks are expected. This fits well to the narrow experimental peaks at 17.9 and 19.2 eV; while the deviation of 2 eV for the calculated shakeup energies is somewhat large though still in the expected range, the energy separation of the two states is well reproduced. Similarly we correlate the next experimental peak (20.1 eV) to the first 5σ–7σ excitation at 21.6 eV. As in N_2 the picture drawn here by our calculation is more complicated due to the occurrence of low lying double excitations of the type $(1\pi)^{-2}(2\pi)^2$, $(4\sigma)^{-1}(5\sigma)^{-1}(2\pi)^2$, and $(5\sigma)^{-2}(2\pi)^2$. The first of these states is placed at 20.8 eV shakeup energy, that is between the two 5σ–6σ satellites. Recalling that this energy may be still too high by, say 3–4 eV due to the incompletely treated relaxation, we expect the actual vertical shakeup energy to be in the range of 17–18 eV. As was discussed in the case of N_2, the double excitations are not expected to be directly apparent in the experimental spectrum as a consequence of very large vibrational broadening. They may nevertheless influence the spectral profile as perturbers of the valence–Rydberg excitations in the vicinity of avoided crossings. Here the static vertical–electronic description based on the Born–Oppenheimer and Franck–Condon approximation no longer applies and allowance must be made for dynamical effects of multistate vibronic interaction.[56]

Towards higher energy the calculated satellite structure becomes increasingly more complicated. There are two series of 5σ–$n\sigma$ excitations converging to the triplet and singlet $(2\sigma)^{-1}(5\sigma)^1$ double ionization continuum, respectively.

Additional states, in particular many more π–π^* and σ–π^* double excitations come into play and interfere with the 5σ–$n\sigma$ series. Even if dynamical effects might be excluded, the present calculation is no longer adequate to account for the spectral details, first since the 3h–2p states are not properly treated, and second, since our approach like any basis set (L^2) approach is not capable of describing Rydberg series except for the very first members.

2. O1s

The calculated O1s binding energy corrected for a relativistic shift (+ 0.4 eV) and the effect of core–valence separation (− 0.4 eV) is 1.0 eV below the experimental value[9] of 542.6 eV. The somewhat poorer agreement here may be due to the considerably larger relaxation shift (about 21 eV) for O1s hole generation, as compared with relaxation energies of about 17 and 13 eV for N1s and C1s. The spectroscopic factor of the O1s main state is 0.61, showing that almost 40% of the partial O1s cross section is distributed upon shakeup and shake-off states.

The present O1s results collected in Table IV draw a picture of the shakeup regime completely different from the case of C1s and N1s discussed above. The triplet-coupled $(S'=1)$ π–π^* satellite is predicted 14.9 eV above the O1s main peak, but with an extremely small spectroscopic factor: if the sudden limit conditions apply this state has only 0.02% of the O1s main peak intensity and will hardly be seen in the photoelectron spectrum. Immediately above the (invisible) triplet-coupled π–π^* satellite a manifold of $(5\sigma)^{-1}(n\sigma)^1$ Rydberg-type shakeup states comes into play. As the result of configuration interaction between these $(5\sigma)^{-1}(n\sigma)^1$ states and the singlet-coupled π–π^* state at higher binding energy there is no longer a distinct state of dominating π–π^* character. The largest π–π^* admixtures, namely 17% and 10% are found in the state Nos. 9 and 11, respectively, and a large portion of spectral strength shows up here. It must be stressed that, of course, the details of this configuration mixing and of the resulting spectral distribution cannot be taken literally from the present calculation. The main reservation

TABLE IV. Calculated O1s spectrum of CO. Ionization energies I_n (eV) and relative intensities P_n of the first 12 $^2\Sigma^+$ states.

No.	Assignment	I_n	P_n
1	$1\sigma^{-1}$	541.56	100(0.61)
2	$1\sigma^{-1}1\pi^{-1}2\pi^1$	$+14.88$	0.02
3	$5\sigma^{-1}6\sigma^1$	15.80	0.001
4	$5\sigma^{-1}6\sigma^1$	17.00	0.4
5	$5\sigma^{-1}7\sigma^1$	17.47	0.2
6	$5\sigma^{-1}7\sigma^1$	18.37	0.9
7	$5\sigma^{-1}8\sigma^1$	20.32	1.5
8	$5\sigma^{-1}8\sigma^1$	20.54	1.5
9	$5\sigma^{-1}n\sigma^1 + 1\pi^{-1}2\pi^1$	21.67	5.9
10	$5\sigma^{-1}n\sigma^1$	22.11	0.6
11	$5\sigma^{-1}n\sigma^1 + 1\pi^{-1}2\pi^1$	22.50	4.3
12	$5\sigma^{-1}n\sigma^1$	24.19	0.01

TABLE V. Shakeup energies eV in zeroth and first order of the $\pi-\pi^*$ and $5\sigma-6\sigma$ satellites.

Satellite $1s^{-1}l^{-1}j^1$	Zeroth order $\epsilon_j - \epsilon_l$	First order	
		C1s	O1s
$1s^{-1}1\pi^{-1}2\pi^1[S'=1]$	21.1	8.8	19.6
$1s^{-1}1\pi^{-1}2\pi^1[S'=0]$	21.1	19.3	30.1
$1s^{-1}5\sigma^{-1}6\sigma^1[S'=1]$	25.5	28.1	20.1
$1s^{-1}5\sigma^{-1}6\sigma^1[S'=0]$	25.5	28.5	20.2

concerns the position of the singlet-coupled $\pi-\pi^*$ state, viewed for the moment as being decoupled from the $(5\sigma)^{-1}(n\sigma)^1$ manifold. Already in the C1s spectrum this state was placed about 2 eV too high by the present calculation. A distinct larger deviation of, say, 3 or 4 eV does not seem unrealistic here in view of the large relaxation in the case of O1s ionization. Also the static vertical picture given by the results in Table IV has possibly to be modified if allowance for dynamical effects is made.

Bearing these last reservations in mind, the present results are, indeed, in good qualitative accord with the recently measured high resolution O1s photoelectron spectrum.[9] First, there is no peak visible at or below the calculated first $\pi-\pi^*$ shakeup energy, in accordance with the predicted small relative intensity. In the previous O1s spectrum by Freund et al.[8] a peak at about 8 eV shakeup energy is present that was related to the triplet-coupled $\pi-\pi^*$ satellite. In view of the present results, this feature apparently is due to an inelastic energy loss of main peak electrons. At higher binding energy, between 17 and 20 eV above the O1s main peak the recent high resolution spectrum shows a dominant group of three relatively closely spaced peaks, the first of which being large and the two others smaller and narrower. We interpret this structure as the result of the interaction between the singlet-coupled $\pi-\pi^*$ state and closely spaced $(5\sigma)^{-1}(n\sigma)^1$ Rydberg states, although our calculation places the centroid of the $\pi-\pi^*$ shakeup intensity about 4 eV too high.

How can the difference of the C1s and O1s shakeup spectra in CO be understood? Let us consider the localization properties of the orbitals in the CO ground state.[13] The 1π orbital in CO is localized more on the side of the O atom while the opposite applies for the 5σ orbital. Thus, a $\pi-\pi^*$ excitation introduces a charge transfer from O to C, while a reversed charge transfer occurs upon $5\sigma-n\sigma$ excitation, assuming here that the unoccupied π^* and $n\sigma$ orbitals have a balanced charge distribution. Depending on whether there is a hole in the C1s or O1s orbital such a charge transfer means either a screening or an antiscreening of the respective core hole reflected by a low or high shakeup energy, respectively. In the case of C1s ionization the $\pi-\pi^*$ satellites are energetically pulled down, whereas the $5\sigma-n\sigma$ satellites are pushed

up. Reversed conditions apply in the case of O1s ionization. Here the $\pi-\pi^*$ states are pushed up, and the $5\sigma-n\sigma$ states are pulled down. As a consequence the second (singlet coupled) $\pi-\pi^*$ component is already immersed in the manifold of the $5\sigma-n\sigma$ Rydberg states.

In first order of perturbation theory with respect to the "frozen" orbital representation of the CO ground state the $\pi-\pi^*$ shakeup energy is given by

$$E_{\pi-\pi^*}^{(1)} = \epsilon_{\pi^*} - \epsilon_\pi + J_{1s,\pi} - J_{1s,\pi^*} - J_{\pi,\pi^*} + \text{exchange.}$$

Considering now the Coulomb integrals J_{kl} of the small SCF calculation specified in Sec. IV A we find a strong dependence of $J_{1s,\pi}$ on the site of the core orbital, namely, a value of ~ 24 eV for O1s and ~ 14 eV for C1s. The Coulomb integral J_{1s,π^*}, on the other hand, is about 14 eV in both cases. By this way the localization property of the occupied π orbital is reflected in the first-order shakeup energy. The corresponding expression for the $5\sigma-6\sigma$ excitation reads

$$E_{5\sigma-6\sigma}^{(1)} = \epsilon_{6\sigma} - \epsilon_{5\sigma} + J_{1s,5\sigma} - J_{1s,6\sigma}$$
$$- J_{5\sigma,6\sigma} + \text{exchange.}$$

Here, $J_{1s,5\sigma}$ assumes a small value (~ 12 eV) for O1s and a large value (~ 21 eV) for C1s. The complete zeroth- and first-order shakeup energies for the triplet and singlet coupled $\pi-\pi^*$ states and the corresponding pair of $5\sigma-6\sigma$ states are listed in Table V. Here, the zeroth-order satellite wave functions and first-order energy expressions of Ref. 54 have been evaluated for the small ($3s/2p$) SCF calculation.

As in N_2, we have performed calculations on both C1s and O1s shakeup states of other symmetries (Tables VI and VII). In each case, the $5\sigma-\pi^*$ ($^2\Pi$) excitation is energetically below the first $^2\Sigma^+$ satellite in the photoelectron spectrum. In the case of O1s a shakeup energy of only 5 eV is predicted for this state. Of course, this again reflects the

TABLE VI. C1s shakeup states of $^2\Pi$, $^2\Delta$, and $^2\Sigma^-$ symmetry.

Symmetry	Assignment	$I_n - I_{1s}$(eV)
$^2\Pi$	$2\sigma^{-1}5\sigma^{-1}2\pi^1$	8.44
$^2\Pi$	$5\sigma^{-1}2\pi^1$	9.20
$^2\Delta$	$2\sigma^{-1}1\pi^{-1}2\pi^1$	9.74
$^2\Sigma^-$	$1\pi^{-1}2\pi^1$	9.83
$^2\Delta$	$1\pi^{-1}2\pi^1$	11.07
$^2\Sigma^-$	$1\pi^{-1}2\pi^1$	11.42
$^2\Pi$	$2\sigma^{-1}4\sigma^{-1}2\pi^1$	13.58
$^2\Pi$	$4\sigma^{-1}2\pi^1$	14.34

TABLE VII. O1s shakeup states of $^2\Pi$, $^2\Delta$, and $^2\Sigma^-$ symmetry.

Symmetry	Assignment	$I_n - I_{1s}$ (eV)
$^2\Pi$	$1\sigma^{-1}5\sigma^{-1}2\pi^1$	5.03
$^2\Pi$	$5\sigma^{-1}2\pi^1$	8.71
$^2\Delta$	$1\pi^{-1}2\pi^1$	14.88
$^2\Sigma^-$	$1\pi^{-1}2\pi^1$	14.90
$^2\Delta$	$1\pi^{-1}2\pi^1$	16.56
$^2\Sigma^-$	$1\pi^{-1}2\pi^1$	16.99
$^2\Pi$	$5\sigma^{-1}3\pi^1$	18.25
$^2\Pi$	$5\sigma^{-1}3\pi^1$	18.41
$^2\Pi$	$4\sigma^{-1}2\pi^1$	19.09
$^2\Pi$	$4\sigma^{-1}2\pi^1$	20.90

ty of the 5σ–π^* excitation with respect to the O1s hole. Analogous observations can be made for the excitations involving the 4σ orbital having more weight on the O side of the molecule.

V. ASPECTS OF THE COMPUTATIONAL METHOD

In the following we briefly discuss some details of the computational method. The first topic concerns the core–valence separation approximation specified in Sec. II E. The error herewith introduced was tested by performing calculations on the level of the much simpler third-order [ADC(3)] scheme, where this approximation can easily be switched on and off. The effect of the core–valence separation approximation on the ionization energies of the N1s, C1s, and O1s single hole main states was an almost uniform enhancement by 0.4 eV. As further analysis shows, the core–valence correlation in the initial ground state is largely cancelled by the contribution of three-core-hole–two-particle states in the ionic states, and the residual shift of 0.4 eV is mainly due to the neglect of two-core-hole–one-particle contributions in the ionic states. Similar tests in the case of satellites already require a fourth-order treatment and were not performed. Probably, shifts of comparable magnitude are to be expected here.

In Table VIII we take a look at the static self-energy part for the core levels of N_2 and CO. As has been mentioned, these quantities enter almost directly the results for the 1s hole main states. Their contribution to the 1s binding energies is approximately given by $\Delta I_{1s} \approx -x_{1s}^2 \Sigma_{1s,1s}(\infty)$, where the spectroscopic factor x_{1s}^2 is of the order of 0.6–0.7. Clearly, a good approximation for these quantities is crucial for accurate 1s binding energies. The direct perturbation expansions evaluated through fourth order of perturbation

TABLE IX. Comparison of second-, third-, and fourth-order approximation schemes: Ionization energies (eV) for the three lowest $^2\Sigma^+$ C1s hole states in CO.

State	2ph-TDA	ADC (3)	ADC (4)	Exp.
$2\sigma^{-1}$	296.8	299.79	296.08	296.2
$2\sigma^{-1}1\pi^{-1}2\pi^1(S'=1)$		310.96	305.19	304.5
$2\sigma^{-1}1\pi^{-1}2\pi^1(S'=0)$		319.60	313.20	311.1

theory (see Table VIII) show large oscillations between third and fourth order and do not allow for a reliable extrapolation. The values employed in the present calculations are listed in the last column of Table VIII. They are obtained in a consistent way from the dynamic self-energy part $M(\omega)$ as described in Sec. II C on the level of the ADC(3) approximation for $M(\omega)$. The resulting static self-energy contributions are complete through fourth order and, moreover, contain infinite partial summations of higher-order terms thereby settling the convergence problem of the finite expansions. The static self-energy part accounts for the change in the static charge distribution of the (neutral) molecule introduced by ground state correlation with respect to the Hartree–Fock charge distribution. In CO, ground state correlation induces a slight charge transfer from O to C (corresponding to the dominant π–π^* double excitation). This means that the C1s and O1s binding energy is decreased and increased, respectively, with respect to the HF result, in accordance with the values of $\Sigma_{1s,1s}(\infty)$ in Table VIII.

A comparison of second-, third-, and fourth-order results for the ionization energies of the three lowest states in the C1s photoelectron spectrum is given in Table IX. The basis set specified in Sec. III and the core–valence separation approximation were employed in these calculations. Obviously, the level of the fourth-order approximation is required if a satisfactory description of core hole main and satellite states is to be reached.

To specify the magnitude of the various ADC(4) contributions, we performed a series of calculations of the N1s states of N_2, omitting a specific contribution in each case. To save computer time these calculations were based on the small (3s/2p) SCF results specified in Sec. IV A. The energy alternations introduced by these modifications for the N1s main state and first satellite are shown in Table X. The largest effect, of course, is due to the matrix elements $C^{(1)}_{jkl,i'j'k'l'm}$ coupling the 2h–1p and 3h–2p states. This introduces a large relaxation shift (here 11.5 eV) for the 2h–1p satellites and indirectly also a considerable shift for the 1s main state. The results in Table X also show that the other

TABLE VIII. Static self-energy part $\Sigma_{1s,1s}(\infty)$ (eV) for the core orbitals of N_2 and CO.

Orbital	Third order	Third + fourth order	ADC (3)
N1s	1.45	0.45	0.71
C1s	2.07	0.18	0.95
O1s	-1.55	$+0.95$	-0.47

TABLE X. Magnitude of specific ADC (4) terms: Alternation (eV) of N1s ionization energies in N_2 upon omitting the specified terms in the ADC (4) scheme. Results of small basis set (3s/2p) calculations.

States	$U^{(3)}_{p,jkl}$	$U^{(2)}_{p,ijklm}$	$C^{(2)}_{jkl,i'j'k'l'}$	$C^{(1)}_{jkl,i'j'k'l'm'}$
$1\sigma_g^{-1}$	$+1.06$	-0.35	$+0.41$	$+2.43$
$1\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1(S'=1)$	$+0.02$	-0.01	-2.10	$+11.56$

contributions are important for accurate 1s binding energies, as all exceed 0.3 eV. For the 2h–1p satellites, on the other hand, the only additional relevant contribution is due to the second-order elements $C_{jkl,j'k'l'}^{(2)}$ accounting for the difference of (neutral) ground state correlation and the contribution of 4h–3p states in the satellite wave functions.

VI. SUMMARY AND CONCLUSIONS

Ionization energies and relative intensities of 1s hole states in N_2 and CO have been studied by means of a complete fourth-order approximation [ADC(4)] for the one-particle Green's function. As the only additional approximation we have introduced the core–valence separation which allowed us to substantially reduce the otherwise numerically very demanding full ADC(4) scheme. In the reduced ADC(4) scheme the ionization energies and spectroscopic amplitudes are calculated directly as eigenvalues and eigenvector components, respectively, of a Hermitean secular matrix defined with respect to the configuration space of 1h, 2h–1p, and 3h–2p cationic states, where one (and only one) hole is in the 1s level.

As usual in the Green's function approach, the present numerical procedures are based on ground state HF results of the neutral molecule (frozen orbitals) and, thus, the effect of electronic relaxation, most important in the case of core level ionization, is not included from the outset, as, e.g., in the usual CI treatment, where the expansions of the cationic states are formulated in terms of relaxed orbitals of a separate HF calculation for the 1s single hole state. This might be viewed as a disadvantage, since an elevated level of approximation is required to yield a proper treatment of the electronic relaxation in the Green's function approach. In the CI approach, on the other hand, a still larger effort is needed, if comparably accurate absolute 1s binding energies are desired. Moreover, the separate CI expansions for the neutral ground state and the cationic states can more easily than usual become unbalanced, since here they are formulated in terms of different sets of orbitals. This also makes it quite tedious to evaluate the spectroscopic factors (relative intensities) of the core hole states. It should be noted that we also considered extending the ADC approximations to a formulation in terms of relaxed orbitals. This introduces additional contributions in the ADC matrices U and C, which can be derived in a straightforward way. On the level of the third-order approximation [ADC(3)] such a version was formulated and studied, but a satisfactory description of 1s ionization could not readily be obtained.

The quality of the ADC(4) description of the 1s ionization is not uniform for the different classes of cationic states. Accurate results have been obtained for the single hole (main) states that are treated consistently through fourth order in the present method. This seems to be an adequate level in accounting for the large relaxation shifts of the 1s binding energies. For the class of 2h–1p shakeup states the ADC(4) results are consistent through second order allowing for a fair account of relaxation in most cases. This can no longer be said for the 3h–2p satellites for which only a consistent first-order treatment is reached on the ADC(4) level. Here discrepancies of several eV between the present results

and experimental values are to be expected. In cases where 3h–2p states mix substantially with 2h–1p states the reliability of the results for the latter is also affected, e.g., in the singlet-coupled π–π^* satellites. Thus, particularly, at higher binding energy the present method might only give a qualitative description of the shakeup profile.

Nevertheless, we hope to have demonstrated here that the regime of atomic and molecular core-level ionization may successfully be accessed by using Green's function techniques, which was previously hindered by the insufficiency of the available third-order approximation schemes. We would like to stress that the numerical effort of the present calculation is comparatively small, namely in the order of magnitude of the familiar single configuration double excitation CI problem. This leaves ample space for larger applications both with respect to the basis sets used and the size of the considered systems.

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