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Application of the open-shell size-consistent self-consistent singles and doubles configuration interaction method to multielectronic transitions in photoelectron spectra

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Abstract. The size-consistent self-consistent matrix dressing method has been applied on an open-shell single-configuration reference state. Once the reference state is converged, several low-lying roots can be obtained for the dressed configuration interaction (CI) matrices of appropriate symmetry. The CI matrices were built with a complete-active-space singles and doubles CI method in order to deal properly with multiconfiguration excited states. The vertical ionization and ionization–excitation transitions are obtained from the difference to the closed shell ground-state energy of the neutral molecule. The method has been applied to NH_3^+ and N_2^+ using atomic natural orbital basis sets and state-average adapted molecular orbitals. Two $^2A_1$ states, very similar and showing great mixing of the $(2a_1^{-1})$ and $(3a_1^{-2}5a_1^1)$ determinants, can be assigned to the broad asymmetric band at 27.6 ± 2 eV in the photoelectron spectrum of NH_3. The possible contribution of a $^2\Pi_g$ $(3\sigma_g^{-2}1\pi_g^1)$ state to the A shake-up peak of N_2 at 24.6 eV is also discussed. Other states, doublets and quadruplets, are reported for both systems up to 30 eV for NH_3 and 37 eV for N_2.

Key words: Matrix dressing – Size-consistency – Vertical ionization potentials – Shake-up peaks – Open shell

1 Introduction

The method known as size-consistent self-consistent singles and doubles configuration interaction, $(SC)^2$–SDCI, [1, 2] is a general procedure to include the nonlinear effects that are lacking in conventional truncated CI and that are responsible for the lack of extensivity of the CI energies [3, 4]. The method is formulated in terms of the intermediate effective Hamiltonian theory [5] as a matrix dressing method. This means that the conventional truncated CI matrix is corrected by the addition of a dressing matrix whose elements, in turn, depend on the wavefunction coefficients of one particular state, the dressing reference state [6]. The dress-then-solve procedure is led to numerical self-consistency through a few iterations. The method provides improved energies and wavefunctions for the dressing reference state. It can be applied to any truncated CI. Note that a single reference dressing (one-state dressing reference) can be applied to a multireference CI (several Slater determinants as CI reference). So, it can be applied to selected CI, or to excitation truncated CI, no matter whether the CI matrices are built starting from a single reference, for example, the standard SDCI method or from a set of reference determinants, for example, the complete-active-space (CAS–SDCI method) [1, 7, 8]. The method has also been successfully applied to energetically selected CI matrices [9].

One of the most striking features of the $(SC)^2$ dressing arises once the convergence has been achieved. The low-lying roots of the dressed CI matrix (as well as their corresponding wavefunctions) also benefit from the cancellation of nonlinear effects that result in size-extensivity [2]. As a consequence, excellent excitation energies and wavefunctions result.

The iterative dressing method was originally conceived for the dressing of closed-shell ground states; however, it can be applied to single-reference open-shell states. As in the closed-shell case, the excited roots of the converged dressed CI matrix are significantly improved in relation to conventional CI. Previous work has shown that excellent vertical ionization potentials (IP) can be obtained for the outer-valence ionization of small molecules using either Dunning's correlation consistent or atomic natural orbital (ANO) basis sets [10].

Several points can be noted.

1. The main condition to have good results with the method is to have an appropriate selection of the

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CAS space. Small active spaces are enough provided that the choice is appropriate.

2. Both single ionizations (i.e., those involving mainly a Koopmans-like process) and multiple ionizations (i.e., those resulting in a mixed ionic state or a shake-up process) can be treated appropriately with the method, because the CAS–SDCI is a very flexible space.
3. The basis set must be at least valence triple zeta. Diffuse or Rydberg basis functions do not have a specially relevant role in the ionization calculations, so the basis sets required to get accurate results can be kept to a reasonable size. This is important because CAS–SDCI spaces can be very large for large basis sets even for small molecules of up to 4–5 first period atoms.

The aim of the present work is to present the results on the vertical ionization and ionization–excitation energies leading to all the low-lying states of the cations that we have found with the open-shell $(SC)^2$–CAS–SDCI method applied to N_2 and NH_3.

2 Method

The matrix dressing technique is a general procedure based on the intermediate Hamiltonian theory (IHT). In the simplest case, a single state, Ψ_M, acts as a dressing reference of IHT. We will assume that one determinant, ϕ_I, is dominant in Ψ_M. In the IHT, the full CI space of the Slater determinants, ϕ, is divided into three parts.

1. The principal space, $S_P = \{\phi_I\}$. The SDCI space is built using S_P as a reference. The determinant ϕ_I necessarily belongs to S_P.
2. The intermediate space, $S_Q = \{\phi_i\}$. It contains all the simple and double excitations on S_P. The S_{PQ} space is the model space of the effective Hamiltonian.
3. All the other excitations belong to the outer space $S_R = \{\phi_\alpha\}$.

The exact wavefunction of the dressing reference state can be written, in the intermediate normalization, as

$$\Psi_M = \phi_I + \sum_{J \neq I} c_J^M \phi_J + \sum_i c_i^M \phi_i + \sum_\alpha c_\alpha^M \phi_\alpha \ . \tag{1}$$

Instead of the full CI eigenequation for one vector labeled as M

$$(\mathbf{H} - \varepsilon_M 1) c_M = 0 \tag{2}$$

we take a truncated CI matrix and correct it by means of a Δ matrix so that

$$(\mathbf{H} + \Delta - E_M 1) c_M = 0 \tag{3}$$

The approached E_M eigenvalue and the truncated c_M eigenvector can be obtained following different definitions of Δ. All of them incorporate effects of the R space that was projected out by the truncation. These effects are estimated from the elements of c_M that remain, i.e., from the coefficients of the model space.

The elements of Δ for the $(SC)^2$ dressing are calculated as follows [2]:

1. All elements of Δ other than Δ_{ii} corresponding to diagonal elements in the intermediate space are zero.
2. If we call D_j^+ the diexcitation operator

$$D_j^+ = a_k^+ a_l^+ a_a a_b \ , \tag{4}$$

then

$$\Delta_{ii} = \sum_{j,\mathrm{COND}} c_j^M H_{Ij} \tag{5}$$

where COND indicates that the following conditions must be followed by the j and I labels for each label i:

1. The determinant ϕ_j can be obtained as $\phi_j = D_j^+ \phi_I$
2. A determinant ϕ_α can be obtained as $\phi_\alpha = D_j^+ \phi_i$
3. $\phi_\alpha \in S_R$

As H is a two-electron operator, in those cases where the operation $D_j^+ \phi_0$ is possible, the matrix element $H_{Ij} = \langle \phi_I | H | \phi_j \rangle$ can be replaced by $\langle \phi_0 | H | D_j^+ \phi_0 \rangle$. This is always the case when ϕ_I is the ground-state closed-shell ϕ_0 determinant.

Note that defined in this way, instead of the traditional one (i.e., based on a closed-shell reference for Ψ_M), Eq. (5) does not impose any special restrictions on ϕ_I, so it can be an open-shell determinant; however, Eq. (5) depends on the c_j^M coefficients, so Eq. (3) needs to be led to self-consistency in an iterative way.

Following a proposal by Dandey et al. [1] and Heully et al. [2] it has been shown that most other low-lying roots of $H + \Delta$, apart from E_M and Ψ_M, are corrected for the lack of size-extensivity. Moreover, once Eq. (3) has been converged, a Δ_{ii} shift can be calculated with Eq. (5) for all H_{ii} elements of the full CI $\mathbf{H}$ matrix, even those belonging to symmetry blocks other than that of ϕ_I.

All the calculations used ANO basis sets [11] and state-averaged molecular orbitals (MOs) from CAS self-consistent-field (SCF) density matrices of spatial symmetry. We call them adapted MOs. The method used was $(SC)^2$–CAS–SDCI in all cases.

3 Results and discussion

3.1 NH_3^+

The ANO basis set was (5*s*4*p*2*d*1*f*/3*s*2*p*1*d*) for N/H. The experimental geometry of ammonia was used (R_{NH} = 1.9124 au, θ_{HNH} = 106.7°), but the calculations were performed using C_s symmetry. The CAS for the MO state average was (8 3), corresponding to (a' a''). The CAS for $(SC)^2$–CAS–SDCI was ($2a_1 3a_1 1e 4a_1 2e$) with seven electrons (eight for the neutral ground state).

The excited states of NH_3^+ are shown in Table 1. The two main lines corresponding to $^2A_1(3a_1^{-1})$ and $^2E(1e^{-1})$ states compare well with the experimental vertical IP

Table 1. Excited states of the NH_3^+ molecule: main and satellite peaks. Size-consistent self-consistent complete-active-space singles and doubles configuration interaction [*(SC)*^{2}*–CAS–SDCI*] calculations with (5*s*4*p*2*d*1*f*/3*s*2*p*1*d*) atomic natural orbital (*ANO*) basis set

Nature of the states		Ionization energy (eV)
Doublets		
$^2A_1$	$(3a_1^{-1})$	10.88
^2E	$(1e^{-1})$	16.67
$^2A_1$	$(3a_1^{-2}4a_1^1)$	23.98
^2E	$(3a_1^{-2}2e^1)$	25.77
$^2A_1$	$(2a_1^{-1}, 3a_1^{-2}5a_1^1)$	26.85
^2E	$(3a_1^{-1}1e^{-1}4a_1^1)$	26.95
^2E	$(3a_1^{-1}1e^{-1}4a_1^1, 3a_1^{-1}1e^{-1}2e^1, 3a_1^{-2}2e^1)$	27.74
$^2A_1$	$(3a_1^{-2}5a_1^1, 2a_1^{-1})$	27.97
^2E	$(3a_1^{-2}3e^1)$	28.13
Quadruplets		
^4E	$(3a_1^{-1}1e^{-1}4a_1^1, 3a_1^{-1}1e^{-1}2e^1)$	25.65
$^4A_1$	$(3a_1^{-1}1e^{-1}2e^1)$	26.36
^4E	$(3a_1^{-1}1e^{-1}2e^1, 3a_1^{-1}1e^{-1}4a_1^1)$	27.79
$^4A_2$	$(3a_1^{-1}1e^{-1}2e^1)$	28.03
^4E	$(3a_1^{-1}1e^{-1}5a_1^1)$	30.23

values [12, 13], 10.85 and 16.4–16.8 eV, (the second band shows large Jahn–Teller distortion) and the IP values of 10.78 and 16.67 eV calculated by Brosolo et al. [13] at the experimental geometry. For the rest of states, we found a sequence similar to the multiconfiguration SCF results of Brammer [14], but our binding energies are better. We point out two results.

1. We find the $^2\mathrm{E}(3a_1^{-2}2e^1)$ state at 25.77 eV instead of at 25.17 eV as given by Brosolo et al. [13].
2. The broad asymmetric experimental band at 27.4 ± 1.5 eV reported by Piancastelli and Cauletti [12] (synchrotron radiation photoelectron spectroscopy) was assigned to a $^2\mathrm{A}_1(2a_1^{-1})$ state at 27.55 eV by Brosolo et al. [13]. Instead, we find two $^2\mathrm{A}_1$ states, showing a greatly mixed nature of the $2a_1^{-1}$ ionization and the $(3a_1^{-2}5a_1^1)$ shake-up. These states occur at 26.85 and 27.97 eV and have very similar nature, which is in agreement with the constant value found over that region for the angular distribution parameter, β [12]. We find four $^2\mathrm{E}$ states in the same region as well as five quadruplet states up to 30.23 eV.

3.2 N_2^+

The ANO basis set was (5*s*4*p*2*d*1*f*). The symmetry was D_{2h}. The CAS for the MO state average was (3 2 2 1 2 1 0 0), which is equivalent to $(2\sigma_g 3\sigma_g 2\sigma_u 1\pi_u 4\sigma_g 3\sigma_u 1\pi_g 2\pi_u)$, and implied ten electrons. Excited states of Σ_g^+, Δ_g, Σ_u^+, Δ_u, Π_u and Π_g symmetries were calculated for N_2^+.

Table 2. Excited states of the N_2^+ molecule: main and satellite peaks. (SC)^2–CAS–SDCI calculations with (5*s*4*p*2*d*1*f*) ANO basis set. Σ_g^+ and Δ_g symmetries

Nature of the states		Ionization energy (eV)
Doublets		
$^2\Sigma_g^+$	$(3\sigma_g^{-1})$	15.41
$^2\Sigma_g^+$	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1, 2\sigma_g^{-1})$	28.82
$^2\Delta_g$	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	29.71
$^2\Delta_g$	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	30.54
$^2\Sigma_g^+$	$(3\sigma_g^{-2}4\sigma_g^1, 2\sigma_u^{-2}3\sigma_u^1)$	32.94
$^2\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2, 2\sigma_g^{-1}, 3\sigma_g^{-2}4\sigma_g^1)$	33.35
$^2\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2, 2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	35.22
$^2\Delta_g$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2, 2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	35.37
$^2\Delta_g$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2)$	35.64
$^2\Delta_g$	$(3\sigma_g^{-1}1\pi_u^{-1}2\pi_u^1)$	35.65
$^2\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-1}2\pi_u^1)$	35.95
Quadruplets		
$^4\Sigma_g^+$	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	25.46
$^4\Delta_g$	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1)$	26.90
$^4\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2)$	30.05
$^4\Delta_g$	$(3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2)$	32.86
$^4\Delta_g$	$(1\pi_u^{-2}3\sigma_g^{-1}1\pi_g^2)$	33.95
$^4\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-1}2\pi_u^1)$	35.30
$^4\Sigma_g^+$	$(3\sigma_g^{-1}1\pi_u^{-1}2\pi_u^1)$	35.44

The CAS for (SC)^2–CAS–SDCI was $(2\sigma_g 3\sigma_g 1\pi_u 1\pi_g)$ with seven electrons (eight for the neutral ground state) for Σ_g^+ and Δ_g, and was $(3\sigma_g 2\sigma_u 1\pi_u 1\pi_g)$ for the Σ_u^+, Δ_u, Π_u and Π_g states. The bond length was $R_{\mathrm{NN}} = 2.074$ au.

The calculated IPs, including both doublet and quadruplet states, are shown in Tables 2–5. The error for the first three main peaks, i.e., the outer valence $\mathrm{X}^2\Sigma_g^+(3\sigma_g^{-1})$, $^2\Pi_u(1\pi_u^{-1})$, $^2\Sigma_u^+(2\sigma_u^{-1})$ lines, is smaller than

Table 3. Excited states of the N_2^+ molecule: main and satellite peaks. (SC)^2–CAS–SDCI calculations with (5*s*4*p*2*d*1*f*) ANO basis set. Σ_u^+ and Δ_u symmetries

Nature of the states		Ionization energy (eV)
Doublets		
$^2\Sigma_u^+$	$(2\sigma_u^{-1})$	18.62
$^2\Sigma_u^+$	$(1\pi_u^{-1}3\sigma_g^{-1}1\pi_g^1, 2\sigma_u^{-1})$	25.27
$^2\Delta_u$	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1)$	26.04
$^2\Delta_u$	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1)$	26.32
$^2\Sigma_u^+$	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1, 2\sigma_u^{-1}, 2\sigma_u^{-1}3\sigma_g^{-1}4\sigma_g^1)$	32.47
$^2\Sigma_u^+$	$(3\sigma_g^{-2}3\sigma_u^{-1}, 2\sigma_u^{-1}3\sigma_g^{-1}4\sigma_g^1, 2\sigma_u^{-2}3\sigma_u^1)$	34.93
$^2\Sigma_u^+$	$(2\sigma_u^{-1}3\sigma_g^{-1}4\sigma_g^1, 3\sigma_g^{-2}3\sigma_u^1, 2\sigma_u^{-2}3\sigma_u^1)$	35.48
$^2\Sigma_u^+$	$(2\sigma_u^{-1}1\pi_u^{-2}1\pi_g^2)$	37.20
Quadruplets		
$^4\Sigma_u^+$	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1)$	22.54
$^4\Delta_u$	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1)$	23.92
$^4\Sigma_u^+$	$(2\sigma_u^{-1}1\pi_u^{-2}1\pi_g^1)$	32.88
$^4\Sigma_u^+$	$(2\sigma_u^{-1}3\sigma_g^{-1}n\sigma_g^1)n = 4, 5, 6$	34.45
$^4\Sigma_u^+$	$(2\sigma_u^{-1}1\pi_u^{-2}1\pi_g^2)$	36.09

Table 4. Excited states of the N_2^+ molecule: main and satellite peaks. (SC)^2–CAS–SDCI calculations with (5*s*4*p*2*d*1*f*) ANO basis set. Π_u symmetry

Nature of the states		Ionization energy (eV)
Doublets		
$^2\Pi_u$	$(1\pi_u^{-1})$	16.88
$^2\Pi_u$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$	28.31
$^2\Pi_u$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1, 3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$	32.06
$^2\Pi_u$	$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2, 3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$	33.92
$^2\Pi_u$	$(3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1)$	34.33
$^2\Pi_u$	$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$	34.42
$^2\Pi_u$	$(3\sigma_g^{-2}2\pi_u^1, 3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1, 2\sigma_u^{-2}2\pi_u^1)$	35.23
$^2\Pi_u$	$(3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1, 3\sigma_g^{-2}2\pi_u^1, 3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$	35.63
$^2\Pi_u$	$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2, 2\sigma_u^{-2}1\pi_u^{-1}1\pi_g^2)$[a]	36.07
$^2\Pi_u$	$(3\sigma_g^{-1}1\pi_u^{-1}5\sigma_g^1, 1\pi_u^{-2}2\pi_u^1, 1\pi_u^{-3}1\pi_g^2)$	37.04
Quadruplets		
$^4\Pi_u$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$	25.03
$^4\Pi_u$	$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2, 2\sigma_u^{-2}1\pi_u^{-1}1\pi_g^2)$	32.59
$^4\Pi_u$	$(3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1)$	33.67
$^4\Pi_u$	$(1\pi_u^{-3}1\pi_g^2)$	36.25
$^4\Pi_u$	$(3\sigma_g^{-1}1\pi_u^{-1}5\sigma_g^1, 1\pi_u^{-2}2\pi_u^1, 1\pi_u^{-3}1\pi_g^2)$	37.00

[a] It is also mixed with $3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1, 3\sigma_g^{-2}2\pi_u^1$

0.2 eV relative to the experimental IPs [15]. The X-ray photoelectron spectrum of N_2 shows a complex structure in the 20–45 eV region [16, 17]. A number of small shake-up bands, usually labeled from A to G, have been recognized apart from the main feature corresponding to the $2\sigma_g^{-1}$ ionization at 37.5 eV. We obtained states up to about 35 eV, so we can try to assign the A–E shake-up bands as summarized in Table 6. The experimental values were estimated from the Al Kα and YMζ X-ray photoelectron spectra in (Fig. 2 of Ref. [17]). Most of these bands are broad (half-width about 1 eV.). Some bands show maxima slightly apart in both spectra. In such cases, we report two experimental values. The most difficult assignment for us is that of peak A. It is usually assigned to a band of ${}^2\Sigma_u^+$ symmetry. We find the second ${}^2\Sigma_u^+$ state to be too high in energy by about 0.7 eV. We do not expect to have errors in the IPs, with the basis set and the method used, greater than 0.3 eV. All the MOs concerned with the dominant excitations enter the CAS. We performed an additional calculation with the Dunning correlation-consistent polarized valence quadruple zeta (*5s4p3d2f1g*) basis set [18] and we obtained a value of 25.35 eV, which would not improve the result; however we found a ${}^2\Pi_g$ state at 24.45 eV. This state was also reported by Herman et al. [19], but with a negligible estimated intensity associated with it. We suggest that the A feature, which is broad and asymmetric towards high binding energies, could be due to both transitions, as indicated in Table 6. We agree with other authors in the assignment of the B peak to ${}^2\Pi_g$ (also expected to be of very low intensity) and the C peak to ${}^2\Sigma_g^+$ [17, 19, 20]. Note, however, that a small contribution to this peak could come from the ${}^2\Pi_u$ $(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$ state at 28.31 eV. The D band was assigned to the third ${}^2\Sigma_u^+$ state in agreement with the energy loss spectra evidence [21]. In the same region we found a ${}^2\Pi_u$ $(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1, 3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$ state at 32.06 eV and a ${}^2\Pi_g(1\pi_u^{-2}1\pi_g^1)$ state at 32.49 eV. We cannot assign the E peak to just one state because we found up to four states close to 34 eV, as indicated in Table 6.

Table 5. Excited states of the N_2^+ molecule: main and satellite peaks. $(SC)^2$–CAS–SDCI calculations with (*5s4p2d1f*) ANOs basis set. Π_g symmetry

Nature of the states		Ionization energy (eV)
Doublets		
${}^2\Pi_g$	$(3\sigma_g^{-2}1\pi_g^1)$	24.45
${}^2\Pi_g$	$(1\pi_u^{-2}1\pi_g^1)$	26.00
${}^2\Pi_g$	$(1\pi_u^{-2}1\pi_g^1)$	27.14
${}^2\Pi_g$	$(1\pi_u^{-2}1\pi_g^1, 2\sigma_u^{-2}1\pi_g^1)$	28.01
${}^2\Pi_g$	$(1\pi_u^{-2}1\pi_g^1)$	32.49
${}^2\Pi_g$	$(2\sigma_u^{-2}1\pi_g^1, 3\sigma_g^{-2}1\pi_g^1, 1\pi_u^{-2}1\pi_g^1)$	34.15
${}^2\Pi_g$	$(2\sigma_u^{-1}3\sigma_g^{-1}2\pi_u^1, 3\sigma_g^{-1}1\pi_u^{-1}3\sigma_u^1)$	36.55
${}^2\Pi_g$	$(2\sigma_u^{-1}3\sigma_g^{-1}2\pi_u^1, 3\sigma_g^{-1}1\pi_u^{-1}3\sigma_u^1)$	36.62
Quadruplets		
${}^4\Pi_g$	$(1\pi_u^{-2}1\pi_g^1)$	25.08
${}^4\Pi_g$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^2)$	30.73
${}^4\Pi_g$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^2)$	33.54
${}^4\Pi_g$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^2)$	35.22
${}^4\Pi_g$	$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^2)$	35.74
${}^4\Pi_g$	$(3\sigma_g^{-1}1\pi_u^{-1}3\sigma_u^1, 3\sigma_g^{-1}2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^2)$	36.15
${}^4\Pi_g$	$(2\sigma_u^{-1}3\sigma_g^{-1}2\pi_u^1, 3\sigma_g^{-1}1\pi_u^{-1}3\sigma_u^1)$	36.71

4 Conclusions

Two possible revisions of previous assignments in the photoelectron spectra of ammonia and nitrogen are suggested. The broad asymmetric band at 27.6 ± 2 eV

Table 6. Shake-up peaks in the 25–35 eV region of the X-ray photoelectron spectra of N_2

Shake-up peaks	Symmetry	This work	Nichols et al.[a]	Herman et al.[b]	Schirmer et al.[c]	Exp.[d]	Nature (this work)
A	${}^2\Pi_g$	24.45	–	–	–	24.6	$(3\sigma_g^{-2}1\pi_g^1)$
	${}^2\Sigma_u^+$	25.27	26.31	25.50	24.78		$(1\pi_u^{-1}3\sigma_g^{-1}1\pi_g^1, 2\sigma_u^{-1})$
B	${}^2\Pi_g$	27.14	26.73	24.64	–	26.9–27.3	$(1\pi_u^{-2}1\pi_g^1)$
C	${}^2\Sigma_g^+$	28.82	29.78	29.44	28.95	28.6–29.1	$(2\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1, 2\sigma_g^{-1})$
	${}^2\Pi_u$	28.31	–	–	–		$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$
D	${}^2\Sigma_u^+$	32.47	37.17	36.28	36.23	31.9–32.4	$(3\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1, 2\sigma_u^{-1}, 2\sigma_u^{-1}3\sigma_g^{-1}4\sigma_g^1)$
	${}^2\Pi_u$	32.06	–	–	–		$(3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1, 3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$
	${}^2\Pi_g$	32.49	28.84	27.19	–		$(1\pi_u^{-2}1\pi_g^1)$
E	${}^2\Pi_u$	33.92	34.13	–	–	34.2	$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2, 3\sigma_g^{-1}2\sigma_u^{-1}1\pi_g^1)$
	${}^2\Pi_g$	34.15	36.80	33.16	–		$(2\sigma_u^{-2}1\pi_g^1, 3\sigma_g^{-2}1\pi_g^1, 1\pi_u^{-2}1\pi_g^1)$
	${}^2\Pi_u$	34.33	–	–	–		$(3\sigma_g^{-1}1\pi_u^{-1}4\sigma_g^1)$
	${}^2\Pi_u$	34.42	–	–	–		$(3\sigma_g^{-2}1\pi_u^{-1}1\pi_g^2)$

[a] Multi Configurational Electron Propagator (MCEP) calculations. See text for reference

[b] Third-order Electron Propagator (EP) with low-order perturbation methods. See text for reference

[c] An approximation to the self-energy. See text for reference

[d] See text for details and references

in the photoelectron spectrum of ammonia is usually assigned to one $^2A_1$ state. Instead, we find two states of the same symmetry at 26.85 and 27.97 eV that show great mixing of the $(2a_1^{-1})$ and $(3a_1^{-2}5a_1^1)$ determinants. On the other hand, the A shake-up band of nitrogen at 24.6 eV is usually assigned to the second $^2\Sigma_u^+$ state. We find the transition to this state to be too high in energy to be the only contribution to this band. The unique state that could fit the observed maxima in the UV photoelectron spectra is the $^2\Pi_g(3\sigma_g^{-2}1\pi_g^1)$ state. Hence, we suggest that this state can contribute to the A band. The assignment of the B–E shake-up peaks in the 25–35 eV region has been briefly discussed.

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