Multiple Solutions of Coupled Cluster Equations: An Application to Molecular Auger Spectra

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A method of determining the multiple solutions of nonlinear multireference coupled cluster (MRCC) equations using the recently introduced eigenvalue independent partitioning (EIP) technique has been applied in this work to find out the Auger diagram and shake-up satellite states of NH_3, PH_3, and HCl at ab initio level. The diagram states are fully size extensive, and the satellites are nearly size extensive with respect to the electrons in a molecule. Strong correlation effects were observed in the states involving inner valence orbital. In most cases, good agreement between the EIP/MRCC results and the experimental and previous theoretical works was found. In particular, controversies about the correct positions of some Auger states have been thoroughly discussed.

I. Introduction

Auger electron spectrum[1−3] is normally described as consisting of the so-called diagram line region and the satellite region. It may be noted that the calculation of the diagram states in the inner valence region and the shake-up satellites of Auger spectra is a nontrivial problem in the conventional multireference coupled cluster (MRCC) method[4−6] and, so also, in MR-MBPT,[7] due to the presence of intruder states[8] that leads to severe numerical divergence. In the MRCC method, one generally solves nonlinear CC equations relative to a multireference function spanning over some pre-defined model subspace P to determine the cluster amplitudes, the variables of the CC equations. The CC amplitudes are then utilized to construct an effective hamiltonian (H_{eff}) matrix which also spans over the P subspace and, hence, upon diagonalization, gives only the roots of the P subspace. These nonlinear CC equations are very susceptible to the numerical instability problem because of their possessing multiple roots. However, the problem was significantly minimized later by proposing the MRCC theory for incomplete models spaces (IMS).[9] Recently, Jankowski et al.[10] have developed numerical methods that use strong damping factor whenever required to find out the “standard solutions” (the main roots) and the “nonstandard solutions” (the alternative roots) of the nonlinear CC equations for atomic open shell problems. Some more recent works[11] on the determination of main and alternative roots may also be referred to in this context.

Mukherjee and co-workers in some recent works[12] have developed an alternative formulation of MRCC theory using eigenvalue independent partitioning (EIP) which converts the nonlinear MRCC equations for any model space (complete or incomplete) into a set of nonhermitian eigenvalue equations. Diagonalization of the so-obtained EIP/MRCC matrix gives all the multiple roots the nonlinear equations in principle do possess. The present work is a rigorous application of this new method on molecular Auger spectra to assess its applicability at the numerical level. In fact, the extensive determination of the Auger shake-up satellites by this method was never pursued before. Here, we have determined the double ionization potentials (DIPs) related to the Auger diagram and shake-up satellite states of NH_3, PH_3, and HCl, using Gaussian basis sets. Our aim is to see whether the diagram states found by us agree with those reported by earlier accurate works, whether the present calculation also reveals that the inner valence regions of each molecule are intensely populated with satellites to indicate the breakdown of independent particle model (IPM) there, and whether our calculated satellites do agree with previous accurate calculations. The work does not include intensity calculation. We have, however, used the SCF intensities available in literature (e.g., for NH_3 and PH_3) to determine the correlated intensities necessary for the evaluation of weighted averages of energies over some states of these molecules. We have presented only those shake-up satellites which have weightage values of the dominant two-hole configuration greater than 0.01, although the number of calculated shake-up satellites is much more than that. All weightages for a molecule relate to a unique orbital basis obtained from the Hartree−Fock calculation on the ground state configuration of that molecule.

The Auger spectra of NH_3 has been largely studied both experimentally[13] and theoretically[14] and thus the molecule offers itself as a good example for testing the workability of our method. In particular, there are accurately calculated shake-up satellites of the molecule available in literature for comparison. In our results, the DIPs for the diagram and satellite states over the entire spectrum are largely consistent with the earlier reported data. HCl also is enriched with sufficient experimental[15] and theoretical[16] data. Here, controversial assignments of some states have been critically discussed. For PH_3, two experiments[17] are known, but the molecule has not been much discussed theoretically so far. Previous INDO(SCF) results, though seemingly to be quite reasonable in explaining the nature of the outer valence region, are not consistent in doing so for the inner valence region of the molecule. This clearly indicates the requirement of a correlated calculation for PH_3. To our knowledge, the EIP/MRCC calculation is the first application

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of an accurate theory for the Auger diagram and shake-up satellite states of the molecule. The reliability of the EIP/MRCC results observed in the cases of NH_3 and HCl encouraged us to make the probable assignments of the experimentally observed peaks and shoulders of its spectrum.

II. Theory and Computational Points in Brief

In the following, we mention only the outlines of the theory necessary to follow the computational procedure of the work. We start from the Fock space Bloch equation:

$$H\Omega P^{(k,l)} = \Omega H_{\mathrm{eff}} \mathrm{P}^{(k,l)}; \quad 0 \le k \le m, 0 \le l \le n \tag{1}$$

where Ω is the valence universal normal ordered wave operator[5] and is expressed as

$$\Omega = \{\exp(S^{[m,n]})\} \tag{2}$$

with

$$S^{[m,n]} = \sum_{k=0}^{m} \sum_{l=0}^{n} S^{(k,l)} \tag{3}$$

The curley bracket in eq 2 denotes normal ordering; $P^{(k,l)}$ stands for the projector for the (kth hole, and the lth particle) model space determinants, holes, and particles defined in respect to the Hartree−Fock vacuum $|\phi_o\rangle$. Ω can also be expressed as

$$\Omega = \exp(S^{(0,0)})\{\exp(S^{[m,n]})\} = \Omega_{\mathrm{c}}^{(\mathrm{o,o})}\, \Omega_{\mathrm{v}}^{[m,n]} \tag{4}$$

where $\Omega_{\mathrm{c}}^{(\mathrm{o,o})}$ stands for the wave operator relating to the core electrons and gives the close shell cluster amplitudes $S^{(0,0)}$. $\Omega_{\mathrm{v}}{}^{[m,n]}$, in which $(k,l) \neq (0,0)$ stands for the wave operator for the valence electrons (two in the present work).

The EIP/MRCC equations for all (k,l) valence ranks were solved hierarchically.[12a−c] First, the closed shell CC calculation (here, done at CCSD level) and then the (1,0) valence rank calculation, which gave IPs and the related cluster amplitudes $S^{(1,0)}$, were performed. Next, we moved on to the (2,0) valence rank calculation to derive the DIPs related to Auger processes. Both of these open shell problems are of complete model space (CMS) type. Thus, for both cases, the closed part of the wave operator followed the equation

$$\Omega_{\mathrm{cl}} = 1 \tag{5}$$

which makes the respective EIP matrix equations noniterative, unlike a general IMS problem.[12c] Following the procedure described earlier,[12a,b] the EIP matrix equation for the (1,0) valence rank was constructed:

$$\begin{bmatrix} Y_{\mathrm{PP}}^{kl} & Y_{\mathrm{PQ}}^{kl} \\ Y_{\mathrm{QP}}^{kl} & Y_{\mathrm{QQ}}^{kl} \end{bmatrix} \begin{bmatrix} X_{\mathrm{PP}}^{kl} \\ X_{\mathrm{QP}}^{kl} \end{bmatrix} = \begin{bmatrix} X_{\mathrm{PP}}^{kl} \\ X_{\mathrm{QP}}^{kl} \end{bmatrix} [\mathrm{E}]^{[1,0]} \tag{6}$$

The eigenvectors of eq 6 gave the $S^{(1,0)}$ cluster amplitudes through the following equation:

$$S^{(1,0)} = X_{\mathrm{QP}}^{kl}\, X_{\mathrm{PP}}^{kl^{-1}} \tag{7}$$

For one valence problems, the EIP/MRCC matrix equations are identical in form with the corresponding matrix equations that appear in CC based linear response theory.[18] All hole orbitals in the calculation were active so that $S^{(1,0)}$ contained no one-body operator $S_1^{(1,0)}$. The cluster operators appearing in the calculation were all two-body operators $S_2^{(1,0)}$ only.

In the (2,0) valence rank,

$$S^{[2,0]} = S_3^{(2,0)} + S_3^{(1,0)} + S_2^{(1,0)} + S^{(0,0)} \tag{8}$$

Since all hole orbitals were active, no two-body operator of the two-valence rank $S_2^{(2,0)}$ also should exist in eq 8. We disregarded the three-body operators of the two valence rank $S_3^{(2,0)}$, as well as of one valence rank $S_3^{(1,0)}$, because these are usually of little importance. The absence of any true two valence operator in $S^{[2,0]}$ reduces the work at the (2,0) valence rank enormously. Thus, one needs only to construct the $H_{\mathrm{eff}}^{[2,0]}$ matrix and not the full EIP matrix. In consequence, the many-body diagrams and the computational labour involved both become substantially reduced than those required for the construction of the EIP matrix.

Now,

$$H_{\mathrm{eff}}^{[2,0]} = H_{\mathrm{eff}}^{(1,0)} + Y_{1\,\mathrm{cl}}^{(2,0)} \tag{9}$$

where

$$H_{\mathrm{eff}}^{(1,0)} = \{\overline{H\,\Omega}_{\mathrm{c}}^{(\mathrm{o,o})}\}_{\mathrm{cl}}^{(1,0)} + \{\overline{\overline{H\,\Omega}_{\mathrm{c}}^{(\mathrm{o,o})}\, S_2^{(1,0)}}\}_{\mathrm{cl}}^{(1,0)} \tag{10}$$

and

$$Y_{1\,\mathrm{cl}}^{(2,0)} = \{\overline{H\,\Omega}_{\mathrm{c}}^{(\mathrm{o,o})}\}_{\mathrm{cl}}^{(2,0)} + \{\overline{\overline{H\,\Omega}_{\mathrm{c}}^{(\mathrm{o,o})} S_2^{(1,0)}}\}_{\mathrm{cl}}^{(2,0)} + \frac{1}{2!}\{\overline{\overline{\overline{H\,\Omega}_{\mathrm{c}}^{(\mathrm{o,o})}\, S_2^{(1,0)}}\, S_2^{(1,0)}}\}_{\mathrm{cl}}^{(2,0)}$$

Thus

$$H_{\mathrm{eff}}^{[2,0]} = Y_{\mathrm{PP}}^{kl}, \text{ for the (2,0) valence rank} \tag{11}$$

The appropriate subset of eigenvectors of the EIP matrix in eq 6 was taken to determine $S_2^{(1,0)}$ from eq 7, which were then utilized to construct the $H_{\mathrm{eff}}^{[2,0]}$ matrix.When the subset of eigenvectors were all of the main IP roots only, the corresponding cluster amplitudes, $S_2^{(1,0)}$, gave the $H_{\mathrm{eff}}^{[2,0]}$ matrix diagonalization of which furnished the DIPs of the Auger diagram states. When the subset of eigenvectors included the eigenvector of a satellite IP in stead of the eigenvector of a main IP root, eq 7 gave the cluster amplitudes of the alternative solutions of the conventional nonlinear MRCC equations at (1,0) valence rank. These then were employed to construct the respective $H_{\mathrm{eff}}^{[2,0]}$ matrix, from diagonalizing of which the DIPs of the relevant Auger shake-up satellites were obtained. Since the main IP roots are both core-electron and valence-electron extensive,[19] the corresponding $S_2^{(1,0)}$ gives Auger diagram states that are both core- and valence-electron extensive. On the other hand, the satellite IP roots are not size extensive with respect to the total number of electrons, but they are size extensive with respect to the core electrons. As a result, the corresponding $S_2^{(1,0)}$ gives Auger shake-up states that are also core-electron extensive. It may be pointed out here that, since the number of valence electrons is much less than the number of core electrons, the error in the size extensivity of the Auger satellite states is only low.

TABLE 1: Auger Diagram States of NH_3

	exptl			exptl DCTS *d*	theoretical relative energy (DIP)				dominant configurations
	a	*b*	*c*		RHF	CI	ADC(2)	MRCC	
$^1A_1$	0.00 (35.36)	0.00 (31.6)	0.00 (34.1)	0.00 (35.3)	0.00 (33.50)	0.00 (35.64)	0.00 (34.19)	0.00 (35.51)	$\mathrm{3a_1^{-2}}$ (0.88)
^3E					2.16	2.29	2.50	2.50	$\mathrm{1e^{-1}3a_1^{-1}}$ (0.87)
^1E	4.73	4.6	4.9	3.6	4.07	3.94	4.16	4.27	$\mathrm{1e^{-1}3a_1^{-1}}$ (0.87)
$^3A_2$					8.23	8.10	8.40	8.37	$\mathrm{1e^{-2}}$ (0.89)
^1E					10.59	9.91	10.18	10.20	$\mathrm{1e^{-2}}$ (0.89)
	10.72	10.5	11.3	9.3		10.48[e]	10.68[e]	10.48[e]	$\mathrm{1e^{-1}2a_1^{-1}}$ (0.01)
$^1A_1$					12.83	11.77	11.81	11.69	$\mathrm{1e^{-2}}$ (0.83) $\mathrm{2a_1^{-2}}$ (0.04)
$^3A_1$	13.45	14.0 15.0	15.0		14.87	14.02	13.90	13.74	$\mathrm{2a_1^{-1}3a_1^{-1}}$ (0.79)
^3E					20.88	19.71	19.65	19.36	$\mathrm{2a_1^{-1}1e^{-1}}$ (0.74) $\mathrm{1e^{-1}3a_1^{-2}4a_1^{1}}$(0.06)
	19.26	19.6	19.1				19.21[e]	19.68[e]	
$^1A_1$					20.78	19.33	19.05	19.79	$\mathrm{2a_1^{-1}3a_1^{-1}}$ (0.79)
^1E	26.54	26.5	26.4		28.55	26.11	25.56	26.35	$\mathrm{2a_1^{-1}1e^{-1}}$ (0.74)
							26.53[e]	26.43[e]	$\mathrm{1e^{-1}3a_1^{-2}4a_1^{1}}$ (0.06)
$^1A_1$	35.56	35.2	34.5		39.72	37.38	36.41	36.41	$\mathrm{2a_1^{-2}}$ (0.60) $\mathrm{2a_1^{-1}3a_1^{-2}4a_1^{1}}$(0.10) $\mathrm{1e^{-2}}$ (0.03), $\mathrm{3a_1^{-2}}$ (0.02)

[a] Reference 13c. [b] Reference 13a. [c] Reference 13b. [d] Reference 13d. [e] Weighted average.

TABLE 2: Auger Shake-up Satellites of NH_3

	RE		
states	MRCC	ADC(2)	dominant configurations (MRCC)
III-band			
$^3A_1$	12.89		*$2a_1^{-1}3a_1^{-1}$ (0.14)*,[a] $\mathrm{2a_1^{-1}3a_1^{-2}4a_1^{1}}$ (0.11), $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.45), $\mathrm{1e^{-1}3a_1^{-2}4e^{1}}$ (0.18)
$^3A_1$	15.41		*$2a_1^{-1}3a_1^{-1}$ (0.08)*, $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.69), $\mathrm{1e^{-1}3a_1^{-2}4e^{1}}$ (0.20)
$^1A_1$	16.37		*$2a_1^{-1}3a_1^{-1}$ (0.10)*, $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.66), $\mathrm{1e^{-1}3a_1^{-2}4e^{1}}$ (0.20) *$3a_1^{-2}$ (0.01)*
IV-band			
$^1A_1$	18.25		*$2a_1^{-1}3a_1^{-1}$ (0.16)*, $\mathrm{2a_1^{-1}3a_1^{-2}4a_1^{1}}$ (0.09), *$3a_1^{-2}$ (0.04)*, $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.42), $\mathrm{1e^{-1}3a_1^{-2}4e^{1}}$ (0.16)
$^3A_1$	20.55		*$2a_1^{-1}3a_1^{-1}$ (0.01)*, $\mathrm{1e^{-2}3a_1^{-1}4a_1^{1}}$ (0.48), $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.29), $\mathrm{1e^{-2}3a_1^{-1}6a_1^{1}}$ (0.06), $\mathrm{1e^{-1}3a_1^{-2}4e^{1}}$ (0.07)
^3E	22.32		*$2a_1^{-1}1e^{-1}$ (0.03)*, $\mathrm{1e^{-1}3a_1^{-2}4a_1^{1}}$ (0.72), $\mathrm{1e^{-2}3a_1^{-1}2e^{1}}$ (0.07)
V-band			
^3E	24.19	23.28	*$1e^{-1}3a_1^{-1}$ (0.05)*, $\mathrm{1e^{-2}3a_1^{-1}2e^{1}}$ (0.48), $\mathrm{1e^{-2}3a_1^{-1}3e^{1}}$ (0.11), $\mathrm{1e^{-1}3a_1^{-2}5a_1^{1}}$ (0.22)
^3E	25.02		*$2a_1^{-1}1e^{-1}$ (0.02)*, $\mathrm{1e^{-3}4a_1^{1}}$ (0.36), $\mathrm{1e^{-3}2e^{1}}$ (0.33), $\mathrm{1e^{-3}6a_1^{1}}$ (0.05), $\mathrm{1e^{-3}4e^{1}}$ (0.08)
^3E	27.11	27.29	*$2a_1^{-1}1e^{-1}$ (0.02)*, $\mathrm{1e^{-3}3e^{1}}$ (0.82)
$^1A_1$	27.14		*$2a_1^{-1}3a_1^{-1}$ (0.01)*, $\mathrm{1e^{-2}3a_1^{-1}4a_1^{1}}$ (0.47), $\mathrm{1e^{-1}3a_1^{-2}2e^{1}}$ (0.28)
		28.65	
^1E	28.31		*$2a_1^{-1}1e^{-1}$ (0.03)*, $\mathrm{1e^{-1}3a_1^{-2}4a_1^{1}}$ (0.69), $\mathrm{1e^{-2}3a_1^{-1}2e^{1}}$ (0.11), $\mathrm{1e^{-1}3a_1^{-2}6a_1^{1}}$ (0.06)
		28.81	
$^3A_1$	31.60		*$2a_1^{-1}3a_1^{-1}$ (0.01)*, $\mathrm{1e^{-1}3a_1^{-2}3e^{1}}$ (0.83)
VI-band			
^1E	31.80	29.35	*$2a_1^{-1}1e^{-1}$ (0.06)*, $\mathrm{1e^{-1}3a_1^{-2}4a_1^{1}}$ (0.10), $\mathrm{1e^{-2}3a_1^{-1}2e^{1}}$ (0.60), *$1e^{-1}3a_1^{-1}$ (0.01)*, $\mathrm{1e^{-2}3a_1^{-1}4e^{1}}$ (0.18)
^1E	32.78		*$1e^{-1}3a_1^{-1}$ (0.01)*, $\mathrm{1e^{-2}3a_1^{-1}2e^{1}}$ (0.17), $\mathrm{1e^{-1}3a_1^{-2}5a_1^{1}}$ (0.47), $\mathrm{1e^{-2}3a_1^{-1}3e^{1}}$ (0.17)
^3E	33.47		*$2a_1^{-1}1e^{-1}$ (0.02)*, $\mathrm{1e^{-3}4a_1^{1}}$ (0.35), $\mathrm{1e^{-3}2e^{1}}$ (0.33), *$1e^{-2}$ (0.02)*, $\mathrm{1e^{-3}4e^{1}}$ (0.08)

[a] 2h configurations in italics.

The eigenvectors of the equation

$$H_{\mathrm{eff}}^{[2,0]}\, X_{\mathrm{PP}}^{kl} = X_{\mathrm{PP}}^{kl}\, E^{[2,0]} \tag{12}$$

and the $S_2^{(1,0)}$ amplitudes gave the weightages of the diagram and shake-up configurations in the *I*th wave function:

$$\Psi_I^{[2,0]} = \Omega_{\mathrm{c}}^{(\mathrm{o,o})}\left\{1 + S_2^{(1,0)} + \frac{1}{2!} S_2^{(1,0)}\, S_2^{(1,0)}\right\} \sum_{\alpha \le \beta} X_{\alpha\beta}^{\mathrm{I}}\, \psi_{\alpha\beta} \tag{13}$$

after having it normalized . In eq 13, $\psi_{\alpha\beta}$ stands for spin adapted functions and α,β for hole orbitals.

III. Results and Discussion

NH_3. The ground state configuration is $^1A_1 = 1a_1^2 2a_1^2 1e^4 3a_1^2$. The four experimentally[13] determined (K−LL) Auger spectra of gas phase ammonia significantly differ in their absolute positions of the origin. The relative energy (RE) values of the three complete spectra[13a−c] are, however, much similar. The spectra determined by double charge transfer spectroscopy (DCTS) experiment[13d] consists of only three lines in the most outervalence region. A number of theoretical calculations[14] are also known among which the most systematic correlated calculation and analysis include the ADC(2)[20] and SDCI results of Tarantelli et al.[14b] In the present EIP/MRCC calculation (Table 1 and Table 2) we, also, have used the same basis and geometry that were taken by them. In most of the cases, good agreements have been observed between the two works, although there are one or two differences also . Among the experimental spectra, those determined by Camilloni et al.[13a] and those due to Shaw et al.[13c] are considered as the two best resolved spectra. It is interesting to note that, in the RE scale, the overall ADC(2) results resemble mainly the spectra of Shaw et al., whereas in the EIP/MRCC calculation, the results agree better with the spectra of Camilloni et al. The EIP/MRCC (35.51 eV) origin (i.e., the absolute value of the peak position of the first band ($3a_1^{-2}$)) is in good accord with most of the literature values, such as those of Shaw et al. (35.36 eV), the DCTS experiment (35.30 eV), and the SDCI (35.64 eV) of Tarantelli et al. The EIP/MRCC results for the two experimentally unobserved states $^3E(1e^{-1}3a_1^{-1})$ and $^3A_2(1e^{-2})$ uniquely agree with ADC(2) and SDCI results. Close agreement is also observed in the case of the second intense band where the SDCI, ADC(2), and EIP/MRCC values all are lower by similar extent than of the experiment. Little difference between the RHF and the correlated results for the above states indicate the validity of the IPM in the outervalence region. However, from the third band onward, correlation becomes increasingly prominent as exhibited by the decreasing weightages of the two-hole configurations in the respective diagram states (Table 1 and ref 14b). The RHF results no longer agree with the experiments which are reproduced only in the correlated results. For illustration, the RHF spacing (by 2.24 eV) between the $^1E(1e^{-2})$ and $^1A_1(1e^{-2})$ diagram states and that (by 2.04 eV) between $^1A_1(1e^{-2})$ and $^3A_1(2a_1^{-1}3a_1^{-1})$ states are so similar that it becomes very difficult to make proper assignments of the experimental results in this energy region.[14b] Contrarily, in ADC(2) and also in SDCI ,the splitting between ^1E and $^1A_1$ is reduced to 1.63 and 1.86 eV, respectively relative to RHF, while that between $^1A_1$ and $^3A_1$ remains practically the same. As a result, one may take the weighted average of the more adjacent ^1E and $^1A_1$ values by using the corresponding SCF intensities and the correlated weightages of the 2h configurations in these states. This gives ADC(2) 10.68 eV, matching very well with the experimental 10.72 eV of Shaw et al. (the respective SDCI weighted average is 10.48 eV). Thus, the two component picture for the deconvolution of the band of Shaw et al. seems to have been explained by the ADC(2) results. This correlated feature has been observed in the EIP/MRCC calculations also, where the relative spacing between ^1E and $^1A_1$ is 1.49 eV and that between $^1A_1$ and $^3A_1$, 2.05 eV. The above weighted average is now 10.48 eV, very close to the experimental 10.50 eV of Camilloni et al. Moreover, contrary to Shaw et al., the deconvolution by Camilloni et al. reports a three-component picture for the third band, the last component with a very low intensity appearing in the far left kinetic energy region of the band. Interestingly, in this part of the band, we found three shake-up satellites all having the weightage for the 2h configuration $2a_1^{-1}3a_1^{-1}$ greater than 0.01, which seems to provide an explanation for the above third low intensity component. Of course, for a clearer picture, determination of the vibrational broadening and of the shake-off satellites are also necessary.

Broadening becomes much more pronounced in the next three bands where the EIP/MRCC calculation reveals the existence of increasing number of shake-up satellites. This is a very common feature being also observed in the inner valence region of theoretical photoelectron spectra[21] of atoms and molecules, where the IPM picture is completely broken down due to strong correlation effects. The RHF results in this region become unreliable because of their drastic overestimation of the diagram states. Using the ADC(2) method, Tarantelli et al. determined the first theoretical satellites of the molecule in the region 22−30 eV. In Table 2, shake-up satellites in the fifth band calculated by the EIP/MRCC method are compared with the corresponding ADC(2) values. Close agreement between the two results is a good indication that the EIP/MRCC method can also be well applied for Auger satellite roots calculation. We have also found shake-up satellites in the fourth unresolved band and in the sixth band. Satellites having very high binding energy have not been reported in the table because of their large dependence on the basis set used and the method of calculation. Furthermore, in all the shake-up satellite states found by us, the dominant 3h−1p configurations contained only the lower lying unoccupied orbitals (p), a fact which was observed in the ADC(2) calculation also.

HCl. The ground state configuration is $^1\Sigma^+ = 1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 4\sigma^2 2\pi^4 5\sigma^2$. The first and complete experimental $L_{2,3}$−MM Auger spectrum of the gas phase HCl had been determined by Aksela et al.[15a] with the aid of electron-beam excitation. Later on, Fournier et al.[15b] determined the Auger spectra of only the higher kinetic energy (KE) region by DCTS technique, while Svensson et al.[15c] did the same using electron impact excitation. On the theoretical side also, Aksela et al.[15a] were the first to do calculation (SDCI) for the diagram states in the outervalence region. Later, Kvalheim[16a] did another SDCI calculation mainly on the diagram states of the entire spectrum. Fournier et al. reported MRD-CI[15b,16b] results along with their experimental findings. However, neither of the two data included the states belonging to the deep inner valence regions. In the EIP/MRCC results, we present the DIPs related to the diagram and shake-up satellite states of the entire spectrum. We used a standard Gaussian basis set such as the one used by Tarantelli et al.[22] for molecules of second-row atoms and it consisted of (12s,8p)[6s,4p][23] on Cl and a 4s [3s][24] on H extended with 2d polarization functions on Cl ($\xi = 1.8, 0.59$)[25] and a p function on H($\xi = 1.0$). The $r_{\mathrm{H-Cl}}$ bond distance taken was 2.40826 au.[26] In the following, we discuss our results in the light of the experimental and previous theoretical results to see the workability of our method.

Due to spin−orbit interaction, there are two possible initial state vacancies[15] on Cl atom (the $2p_{1/2}$ state with binding energy 209.03 eV and the $2p_{3/2}$ state with binding energy 207.40 eV) giving rise to two overlapping series (L_2 and L_3) of spectra for HCl. In Table 3, the EIP/MRCC DIPs of the diagram states relative to the EIP/MRCC origin (DIP = 35.03 eV, KE = 174.03 eV) are given. Table 4 shows the relative energies (RE) of all shake-up satellite DIPs. Both kinds of DIPs may be subtracted from the two initial state binding energies to generate the corresponding L_2- and L_3-kinetic energies. Let us first consider the spectral origins of various results. The experimental origin was found at 173.3 eV.[15] The best theoretical origin is the MRD-CI value[15b,16b] namely, DIP = 35.81 eV, and KE = 173.22 eV. The difference between our result and the MRD-CI result is not unexpected because the latter calculation employed a much bigger basis than ours and took a full CI estimate relative to that basis, whereas in our calculation we considered only the most dominating two-body cluster operators, $S_2^{(1,0)}$.

There is a visible agreement between the EIP/MRCC REs and the experimental as well as other theoretical REs of the next three bands of the outervalence region. Unlike the previous bands, the fourth band (RE = 3.8−7.8 eV) is somewhat broad which may be due to the presence of four diagram states [L_2− and L_3−KE components of $^{1,3}\Pi(5\sigma^{-1}2\pi^{-1})$ states]. Vibrational transitions may also be responsible for the broadening. Neither the EIP/MRCC nor any other calculation does report of any satellite lying in the band. Contrary to what Aksela et al.[15b] and Kochur et al.[16d] reported, our calculation reveals that the diagram state $^1\Sigma^+(5\sigma^{-2})$ (RE = 10.65 eV) does not belong to the fourth but rather belongs to the fifth low intensity broad

TABLE 3: Auger Diagram States of HCl

	exptl			theoretical relative energy (DIP)				dominant
states	*a*	*b*	*c*	SDCI	MRDCI	*a*	MRCC	configuration (MRCC)
$^3\Sigma^-$	0.00 (35.73)	0.00 (35.9)	0.00 (35.73)	0.00[e]	0.00 (35.81)	0.00[e]	0.00 (35.03)	$2\pi^{-2}$ (0.89)
$^1\Delta$	1.77	1.50	1.60	1.80	1.54	1.71	1.80	$2\pi^{-2}$ (0.91)
$^1\Sigma^+$	2.67	2.70	3.10	3.00	2.84	2.94	2.64	$2\pi^{-2}$ (0.85), $4\sigma^{-2}$ (0.02) $5\sigma^{-2}$ (0.01)
$^3\Pi$	3.48		4.50	3.90	3.86	4.00	4.01	$5\sigma^{-1}2\pi^{-1}$ (0.89)
$^1\Pi$	4.63	5.00		5.50	5.26	5.51	5.62	$5\sigma^{-1}2\pi^{-1}$ (0.89)
$^1\Sigma^+$	9.70[d]	9.70		10.60	10.24		10.65	$5\sigma^{-2}$ (0.84), $4\sigma^{-2}$ (0.03)
$^3\Pi$	13.50			13.30			13.75	$4\sigma^{-1}2\pi^{-1}$ (0.64) $2\pi^{-3}6\sigma^1$ (0.08) $2\pi^{-3}7\sigma^1$ (0.05)
$^3\Sigma^+$				19.70			17.29	$4\sigma^{-1}5\sigma^{-1}$ (0.58) $5\sigma^{-1}2\pi^{-2}6\sigma^1$ (0.15) $5\sigma^{-1}2\pi^{-2}7\sigma^1$(0.08)
$^1\Pi$	18.5			18.70			19.76	$4\sigma^{-1}2\pi^{-1}$ (0.65) $2\pi^{-3}6\sigma^1$ (0.08) $2\pi^{-3}7\sigma^1$ (0.05)
$^1\Sigma^+$	25.0			22.50			23.48	$4\sigma^{-1}5\sigma^{-1}$ (0.55) $4\sigma^{-2}$ (0.02) $5\sigma^{-1}2\pi^{-2}6\sigma^1$ (0.14) $5\sigma^{-1}2\pi^{-2}7\sigma^1$ (0.08)
$^1\Sigma^+$				29.40			31.59	$4\sigma^{-2}$ (0.37), $5\sigma^{-2}$ (0.01) $4\sigma^{-1}5\sigma^{-1}$ (0.01) $2\pi^{-2}$ (0.03) $4\sigma^{-1}2\pi^{-2}6\sigma^1$ (0.19) $4\sigma^{-1}2\pi^{-2}7\sigma^1$ (0.11)

[a] Reference 15a. [b] Reference 15b. [c] Reference 15c. [d] Reference 16a. [e] Represents the lowest energy of $HCl^{+2} = -458.9521$ or -458.8649 au, respectively.

TABLE 4: Auger Shake-up Satellites of HCl

states	relative energies (DIP)	dominant 2h configurations
band-V		
$^1\Sigma^+$	11.78	$5\sigma^{-2}$ (0.23)
$^3\Pi$	13.73	$4\sigma^{-1}2\pi^{-1}$ (0.34), $5\sigma^{-1}2\pi^{-1}$ (0.01)
$^3\Sigma^+$	14.44	$4\sigma^{-1}5\sigma^{-1}$ (0.18)
$^3\Pi$	15.25	$4\sigma^{-1}2\pi^{-1}$ (0.35)
band-VI		
$^1\Sigma^+$	19.28	$5\sigma^{-2}$ (0.13), $4\sigma^{-1}5\sigma^{-1}$ (0.11)
$^1\Pi$	19.34	$4\sigma^{-1}2\pi^{-1}$ (0.27)
$^1\Pi$	19.92	$4\sigma^{-1}2\pi^{-1}$ (0.19)
$^1\Pi$	20.13	$4\sigma^{-1}2\pi^{-1}$ (0.22)
$^3\Sigma^+$	20.79	$4\sigma^{-1}5\sigma^{-1}$ (0.23)
$^1\Pi$	21.21	$4\sigma^{-1}2\pi^{-1}$ (0.35)
band-VII		
$^3\Pi$	22.71	$4\sigma^{-1}2\pi^{-1}$ (0.025)
$^1\Sigma^+$	25.91	$4\sigma^{-1}5\sigma^{-1}$ (0.19), $4\sigma^{-2}$ (0.015)
$^3\Pi$	27.69	$4\sigma^{-1}2\pi^{-1}$ (0.15)
$^1\Pi$	28.44	$5\sigma^{-1}2\pi^{-1}$ (0.01)
$^1\Pi$	28.83	$4\sigma^{-1}2\pi^{-1}$ (0.025)
$^1\Sigma^+$	29.17	$4\sigma^{-2}$ (0.30), $2\pi^{-2}$ (0.016), $4\sigma^{-1}5\sigma^{-1}$ (0.01) $5\sigma^{-2}$ (0.01)
band-VIII		
$^1\Sigma^+$	30.01	$4\sigma^{-2}$ (0.17)
$^1\Sigma^+$	30.52	$4\sigma^{-2}$ (0.37), $2\pi^{-2}$ (0.01), $4\sigma^{-1}5\sigma^{-1}$ (0.01)
$^1\Sigma^+$	30.72	$4\sigma^{-2}$ (0.19)
$^3\Sigma^+$	31.81	$4\sigma^{-1}5\sigma^{-1}$ (0.13)
$^1\Pi$	32.55	$4\sigma^{-1}2\pi^{-1}$ (0.14)

band (RE 8.5−17 eV). Our result agrees with Kvalheim's SDCI[16a] and the MRDCI values[15b,16b] which were confirmed by the DCTS experiment of Fournier et al.[15b] also. Besides the L_2− and L_3−KE components of the $^1\Sigma^+(5\sigma^{-2})$ state, there are also present, in the band, L_2− and L_3−KE components of the $^3\Pi(4\sigma^{-1}2\pi^{-1})$ state and L_2-component of the $^3\Sigma^+(4\sigma^{-1}5\sigma^{-1})$ state. Kochur et al.[16d] reported that shake-off satellites contribute to the broadening of the band. We found in the band a number of L_2- and L_3-shake-up satellites also, all having weightage of the dominant 2h configuaration greater than 0.01. Thus the presence of the above diagram states and the shake-up and shake-off satellites provides a reasonable explanation for the broadening of the band. In Table 3, the EIP/MRCC results show that from the $^3\Pi(4\sigma^{-1}2\pi^{-1})$, (RE = 13.75 eV) state onward, the weightages of the 2h configurations in the diagram states, all involving a hole in the inner valence orbital 4σ, gradually decrease. All bands from the fifth onward are more or less broad and of low intensities. In fact, we found all these bands to be intensely populated with L_2- and L_3-shake-up satellites (Table 4), which indicate the existence of strong correlation effects and consequent breakdown of the IPM in the inner valence regions. The EIP/MRCC results for the diagram states in the inner valence region are close to the only available corresponsing theoretical values of Kvalheim, although there is a difference between the order of appearances of some states in the two works. Where we found the order of appearance for these states as $^3\Pi(4\sigma^{-1}2\pi^{-1}) < {}^3\Sigma^+(4\sigma^{-1}5\sigma^{-1}) < {}^1\Pi(4\sigma^{-1}2\pi^{-1}) < {}^1\Sigma^+(4\sigma^{-1}5\sigma^{-1})$, increasing from lower to higher DIPs, Kvalheim et al. reported that to be as $^3\Pi < {}^1\Pi < {}^3\Sigma^+ < {}^1\Sigma^+$. For reasons given below, the EIP/MRCC order of appearance seems to be more appropriate. Firstly, the spectrum of HCl molecule is much similar to that of isoelectronic Ar atom. The spectrum of HCl ion, in the first approximation, can be understood in terms of the (doubly ionized) energy level structure of Ar perturbed by one proton remaining at an equilibrium distance equal to the bond distance of HCl from the Ar core . This view was followed by Aksela et al.[15a] in their analysis. Thus, the $(3s^{-1}3p^{-1})^1P$ and $(3s^{-1}3p^{-1})^3P$ in Ar correlate respectively to $(4\sigma^{-1}5\sigma^{-1})^1\Sigma^+$ and $(4\sigma^{-1}2\pi^{-1})^1\Pi$ and to $(4\sigma^{-1}5\sigma^{-1})^3\Sigma^+$ and $(4\sigma^{-1}2\pi^{-1})^3\Pi$ states in HCl. For this, the singlet−triplet splitting in Ar (by 5.0 eV)[16a] should also roughly be observed in both pairs $(^1\Sigma^+,{}^3\Sigma^+)$ and $(^1\Pi,{}^3\Pi)$, in HCl. The EIP/MRCC corresponding singlet−triplet energy differences are ∼6.0 eV each (Table 3), whereas the SDCI values of Kvalheim are 3.4 and 5.4 eV, respectively .It may also be emphasized that this EIP/MRCC characteristic has also been reflected in the correspondences between the pair of states (^3P, ^1D, $3p^{-2}$ with energy difference 2.0 eV) in Ar and the pair

TABLE 5: Direct (*D*) and Exchange (*E*) Integrals (in eV) of H_{eff} or *H* for the Different Singlet−Triplet Pairs (in Relative Energy Scale)

		RHF		MRCC		SDCI	
	states	*D*	*E*	*D*	*E*	*D*	*E*
NH$_3$	$1e^{-1}3a_1^{-1}$	3.115	0.955	3.385	0.885	3.115	0.825
	$1e^{-2}$	9.41	1.18	9.285	0.915	9.005	0.905
		10.53	2.30	10.03	1.66	9.935	1.835
	$2a_1^{-1}3a_1^{-1}$	17.82	2.95	16.765	3.025	16.675	2.655
	$2a_1^{-1}1e^{-1}$	24.715	3.83	22.855	3.495	22.91	3.20
HCl	$5\sigma^{-1}2\pi^{-1}$			4.815	0.80	4.70	0.80
	$4\sigma^{-1}2\pi^{-1}$			16.755	3.005	16.00	2.70
	$4\sigma^{-1}5\sigma^{-1}$			20.38	3.095	21.10	1.40
PH$_3$	$2e^{-2}$	3.50	0.80	3.985	0.815		
		4.30	1.60	4.96	1.79		
	$4a_1^{-1}5a_1^{-1}$	10.50	0.90	9.075	2.005		
	$4a_1^{-1}2e^{-1}$	13.45	1.25	12.945	2.765		

of states ($^3\Sigma^-$, $^1\Delta$, $2\pi^{-2}$ with energy difference 1.80 eV) or ($^3\Pi$,$^1\Pi$, $5\sigma^{-1}2\pi^{-1}$ with energy difference 1.61 eV) in HCl. Secondly, the singlet and triplet energies for a state are respectively equal to the sum and the difference of the direct integral $\langle\psi_{\gamma\delta}|H_{\mathrm{eff}}|\psi_{\alpha\beta}\rangle$ and the exchange integral $\langle\psi_{\delta\gamma}|H_{\mathrm{eff}}|\psi_{\alpha\beta}\rangle$ where $\psi\alpha\beta$, etc., refer to the spin-adapted functions produced from the 2h configurations $\phi_{\alpha\beta}$, etc. Assuming that the singlet−triplet energies give roughly an estimate of the diagonal elements of the corresponding H_{eff} (in EIP/MRCC) or H (in SDCI) matrices, it is possible to calculate the direct and exchange integrals both for EIP/MRCC and for SDCI from their corresponding singlet−triplet values in Table 3. It reveals that, in the case of EIP/MRCC, as one goes downward in Table 3, the direct as well as the exchange integrals keep on increasing while, in the case of SDCI, although the direct integrals always increase, the exchange integrals do not (Table 5). This charateristic was also observed in NH$_3$ from which we may justify our order of appearance of ^{3}E($2a_1^{-1}1e^{-1}$) and ^{1}A$_1$($2a_1^{-1}3a_1^{-1}$) in that molecule. Thirdly, the limited CI calculations (such as SDCI) are size inextensive[27] which may be responsible for the error in the results when the correlation becomes strong.

The last two bands (seventh and eighth) are very strongly affected by satellite processes which indicate the existence of more pronounced correlation there.

PH$_3$. The ground state configuration of this molecule is $1a_1^2 2a_1^2 1e^4 3a_1^2 4a_1^2 2e^4 5a_1^2$. Two experiments on the L$_{2,3}$−MM Auger spectrum of gas phase PH$_3$ are known. A high-resolution spectrum (A)using 0.4−2.1 MeV He$^+$ ion bombardment on phosphine gas was reported by Ariyasinghe et al.[17a] In yet another experiment, Larkins et al.[17b] recorded the Auger spectrum(B) of phosphine gas following 2p core-hole ionization of the P atom induced by photons with energy in the range 150−170 eV. They also did simultaneously a RHF calculation of the positions and relative intensities (RI) of the Auger diagram states of the molecule employing the semiempirical INDO molecular orbital approximation . Tables 6 and 7 respectively show the EIP/MRCC results of the diagram and the satellite states of the molecule obtained by using Gaussian basis sets. The basis consisted of (12s,8p)[6s,4p][23] for P and a 4s[2s][24] for H with two d functions on P (ζ = 0.825, 0.275)[25] and a p function on H (ζ = 1.0). The geometry was taken from ref 26. For analysis, we use the RHF/INDO RIs, which, although approximate, are reasonably good at least in the outer-valence region, to determine correlated intensities required for the weighted average of energy calculations. The initial state of the Auger processes in PH$_3$ is a 2p$_{1/2}$(L$_2$) or 2p$_{3/2}$(L$_3$) vacancy on the P atom with an energy splitting of 0.90 eV which arises from spin−orbit coupling, the binding energies being 137.95 and 137.05 eVs, respectively. As in HCl, in PH$_3$ also two overlapping L$_2$- and L$_3$-series of Auger diagram and satellite lines do appear. The statistical ratio (1:2) of the intensities of L$_2$ and L$_3$ lines, implies that a L$_3$-component would be 2 times more intense than the L$_2$-component of a state. Since there is no correlated DIP data available in literature, we shall make the analysis in terms of Auger electron kinetic energies (KE) in the relative energy (RE) scale, as it is actually the KE which represents the experimental spectrum. The number of experimentally observed peaks is much less than that of the diagram states, 11 each, of the L$_2$- and L$_3$-series. So whenever required we take the weighted averages of the energies of the closely-lying states.

The deconvolutions of the two experimental spectra differ in the total number of peaks and also in the reported respective positions. The spectrum (A) shows more lines than the spectrum (B)—some of the lines in (A) may be representing Auger satellites. The first step in the analysis is the determination of the absolute position of the origin of the spectrum which relates to the peak position of the first intense band in the higher KE region. Experiment of Larkins et al. found this peak position at 104.5 eV. Their INDO calculation of RI shows that the first peak relates mainly to the ^{3}E($2e^{-1}5a_1^{-1}$) diagram state, which is just preceeded by the ^{1}A$_1$($5a_1^{-2}$) state with a much lower RI value. They described the ^{3}E state as the origin of the spectra. They took the average (137.50 eV) of L$_2$- and L$_3$-binding energies as the core-hole IP and subtracted the DIP of the ^{3}E state from this to find out the theoretical KE (105.2 eV) for the state. For an ab initio size-extensive calculation, one must however consider the L$_2$- and L$_3$-core-hole IPs individually. In the EIP/MRCC calculations, the L$_3$-component of the ^{3}E($2e^{-1}5a_1^{-1}$) state corresponds to a KE = 104.4 eV. This is immediately followed by the L$_2$−^{1}E($2e^{-1}5a_1^{-1}$) at a RE = 0.09 eV. From their combined intensities, we may assume the origin to be at 104.4 eV. The experiment of Ariyasinghe et al. also found the first peak at KE = 104.3 eV which they described as the ^{1}A$_1$($5a_1^{-2}$) state. Their theoretical assignments of the peaks do not, however, seem to be much accurate as the method they applied gave only a rough estimate of the positions of the diagram states. The lower intensity ^{1}A$_1$($5a_1^{-2}$) state in EIP/MRCC calculation appears at the KE 106.38 eV (L$_2$) and 105.48 eV (L$_3$) where the more intense L$_3$−^{1}A$_1$ component is very close to the L$_3$-^{3}E state of much higher intensities and is, as such, not sufficient distinct from that state to consider it as the origin of the spectrum. The first band is, however, considerably broad over a range of 108−102 eV KE, although it does not contain any shake-up satellites. This is so because of the presence of a number of diagram states such as the L$_2$− and L$_3$−^{1}A$_1$, L$_2$− and L$_3$−^{3}E , L$_2$− and L$_3$−^{1}E states, and the L$_2$−^{3}A$_2$($2e^{-2}$) state. Vibrational excitations, which are more pronounced in PH$_3$ than in HCl, may, in addition, be responsible for this broadening.

The second band ranges over KE 102−97 eV which in the RE scale represents the range (3.0−7.5 eV). Spectrum (A) exhibits two peaks at RE = 3.7 and 6.2 eV. In contrast, spectrum (B) shows only one deconvoluted line at 4.4 eV RE, although the actual experimental curve of (B) shows a peak at 4.3 eV followed by a shoulder at around 6.9 eV. Since a number of diagram states belong to this band (Table 6), we take the weighted averages of the REs of the closely lying lines to have the peak positions at RE = 4.10 and 6.60 eV in the EIP/MRCC results. Thus the weighted average which is obtained by using

TABLE 6: Auger Diagram States of PH_3

	relative KE (eV)							
states	exptl[a]	exptl[b]	INDO[b]		MRCC	peaks	RI INDO[b]	dominant configurations (MRCC)
				L_2	−1.98			
$^1A_1$			−0.6	L_3	−1.08		35.9	$5a_1^{-2}$ (0.87), $2e^{-2}$ (0.01)
				L_2	−0.90			
^3E	0.0[c]	0.0[d]	0.0[e]	L_3	0.0[f]		100.0	$2e^{-1}5a_1^{-1}$ (0.86) $2e^{-2}$ (0.03)
				L_2	0.09			
^1E			2.6	L_3	0.99		55.0	$2e^{-1}5a_1^{-1}$ (0.86) $2e^{-2}$ (0.03)
				L_2	2.27			
$^3A_2$			2.7				49.0	$2e^{-2}$ (0.89)
				L_3	3.17			
	3.7	4.4				4.10[g]		
				L_2	3.9			
^1E			4.3				49.7	$2e^{-2}$ (0.78) $4a_1^{-1}2e^{-1}$ (0.07) $2e^{-1}5a_1^{-1}$ (0.02)
				L_3	4.8			
				L_2	5.85			
$^1A_1$			5.9				30.8	$2e^{-2}$ (0.74), $4a_1^{-2}$ (0.07) $4a_1^{-1}5a_1^{-1}$ (0.02)
				L_3	6.75			
	6.2	6.9*				6.60[g]		
				L_2	6.17			
$^3A_1$			9.6				27.3	$4a_1^{-1}5a_1^{-1}$ (0.64) $2e^{-1}5a_1^{-2}3e^1$ (0.20)
				L_3	7.07			
				L_2	9.28			
^3E			12.2				53.8	$4a_1^{-1}2e^{-1}$ (0.65) $2e^{-2}5a_1^{-1}3e^1$ (0.20)
				L_3	10.18			
	9.7	9.8				10.18[g]		
				L_2	10.18			
$^1A_1$			11.4				22.6	$4a_1^{-1}5a_1^{-1}$ (0.64) $2e^{-1}5a_1^{-2}3e^1$ (0.20) $4a_1^{-2}$(0.01)
				L_3	11.08			
				L_2	14.81			
^1E	16.4	17.1	14.7			15.92[h]	52.4	$4a_1^{-1}2e^{-1}$ (0.60) $2e^{-2}5a_1^{-1}3e^1$ (0.18) $2e^{-2}$ (0.03), $2e^{-1}5a_1^{-1}$ (0.01)
				L_3	15.71			
				L_2	20.15			
$^1A_1$	21.6	22.9	23.3				12.0	$4a_1^{-2}$ (0.47), $2e^{-2}$ (0.04) $4a_1^{-1}2e^{-1}5a_1^{-1}3e^1$ (0.28) $5a_1^{-2}$ (0.01)
				L_3	21.05			

[a] Reference 17a. [b] Reference 17b. [c] 104.3 eV. [d] 104.5 eV. [e] 105.2 eV. [f] 104.4 eV. [g] Weighted average. [h] Weighted average of the ^1E diagram and satellite states in band IV (following ref 14b).

the statistical ratio (L_2:L_3) of INDO intensities of $L_3-{}^3A_2(2e^{-2})$, L_2- and $L_3-{}^1E(2e^{-2})$ states represent a peak position at 4.10 eV which is close to the experimental (A) peak at 3.7 eV. Similarly, the weighted average of the L_2- and $L_3-{}^1A_1(2e^{-2})$, and the L_2- and $L_3-{}^3A_1(4a_1^{-1}5a_1^{-1})$ states gives a peak position at 6.6 eV,which is close to the corresponding values of the two different experiments. The third band ranging over 7.5−13.5 eV is of still lower intensity and contains a peak at 9.7−9.8 eV in both the deconvoluted results. Again we take the weighted average of the REs of the closely lying L_2- and L_3-components of the diagram states $^3E(4a_1^{-1}2e^{-1})$ and $^1A_1(4a_1^{-1}5a_1^{-1})$ of the EIP/MRCC results. The peak position thus obtained corresponds to a RE 10.18 eV which agrees well with the experimental value. From Table 5 we see that for PH_3 also, the EIP/MRCC order of appearance of the diagram $^3A_1(4a_1^{-1}5a_1^{-1})$, $^3E(4a_1^{-1}2e^{-1})$, $^1A_1(4a_1^{-1}5a_1^{-1})$, and $^1E(4a_1^{-1}2e^{-1})$ states is consistent with that for the inner valence diagram states of NH_3 and HCl. It is clear from Table 5, that the EIP/MRCC order of appearance of these states is more reasonable than that obtained by the INDO(SCF) calculation which are not consistent in this region. From the third band onwards Auger satellite processes start appearing in the spectrum indicating the strong correlation effect in the inner valence region. The peak observed at 12.6 eV in the high-resolution spectrum (A) is most probably due to the satellite $^3E(4a_1^{-1}2e^{-1})$ at 12.11 eV and the satellites $^3A_1(4a_1^{-1}5a_1^{-1})$ at 12.25 and 12.75 eVs.

In the fourth band (RE = 13.5−21.0 eV), two experimental peaks have been reported in spectrum (A). The first peak appears at 16.4 eV, while the second appears at 18.9 eV. The deconvolution of Larkins et al. reports, instead, of one peak only at 17.1 eV which seems to be due to the low resolution of the spectrum. According to the EIP/MRCC results, the peak at 16.4 eV represents the diagram state $^1E(4a_1^{-1}2e^{-1})$. Table 7 shows that as many as thirteen L_3-shake-up satellite states belong to the fourth band which indicates the presence of strong correlation effect. It is also apparent that the L_2- and L_3-shake-up satellites with the dominant 2h configuration $^3E(4a_1^{-1}2e^{-1})$ at RE = 17.88−19.12 eV contribute to the experimental low-intensity peak at 18.9 eV. The last band occuring at 20.4 eV onward have still lower intensity due to yet more pronounced correlation effects. As in the case of the previous two molecules, the EIP/MRCC results for the diagram states of the last band are not highly accurate.

TABLE 7: Auger Shape-up Satellites of PH_3

		L_3-relative KE (eV)		
	states	MRCC	exptl[a]	dominant 2h configurations
band-III	$^3A_1$	8.35		$4a_1^{-1}5a_1^{-1}$ (0.14)
	$^1A_1$	9.80		$4a_1^{-1}5a_1^{-1}$ (0.16), $2e^{-2}$ (0.02), $5a_1^{-2}$ (0.02)
	$^3A_1$	10.20		$4a_1^{-1}5a_1^{-1}$ (0.13)
	$^1A_1$	11.12		$2e^{-2}$ (0.015), $4a_1^{-1}5a_1^{-1}$ (0.01)
	^3E	12.11		$4a_1^{-1}2e^{-1}$ (0.13)
	$^3A_1$	12.25		$4a_1^{-1}5a_1^{-1}$ (0.01)
			12.6	
	$^3A_1$	12.74		$4a_1^{-1}5a_1^{-1}$ (0.11)
	^3E	13.55		$4a_1^{-1}2e^{-1}$ (0.05)
band-IV	$^3A_1$	14.49		$4a_1^{-1}5a_1^{-1}$ (0.05)
	$^1A_1$	14.58		$4a_1^{-1}5a_1^{-1}$ (0.11), $2e^{-2}$ (0.03)
	$^1A_1$	14.96		$4a_1^{-1}5a_1^{-1}$ (0.07)
	^3E	15.83		$4a_1^{-1}2e^{-1}$ (0.11)
	$^1A_1$	16.15		$4a_1^{-1}5a_1^{-1}$ (0.05)
	^1E	16.92		$4a_1^{-1}2e^{-1}$ (0.05)
	^1E	17.36		$4a_1^{-1}2e^{-1}$ (0.05)
	^3E	17.88		$4a_1^{-1}2e^{-1}$ (0.06)
	^3E	18.48		$4a_1^{-1}2e^{-1}$ (0.02)
	^3E	18.66	18.9	$4a_1^{-1}2e^{-1}$ (0.01)
	^3E	19.12		$4a_1^{-1}2e^{-1}$ (0.11)
	^1E	19.18		$4a_1^{-1}2e^{-1}$ (0.11)
band-V	^1E	21.21		$2e^{-1}5a_1^{-1}$ (0.03)
	^1E	22.71		$4a_1^{-1}2e^{-1}$ (0.11)
	^1E	24.04	24.3	$4a_1^{-1}2e^{-1}$ (0.05)
	$^3A_1$	24.57		$4a_1^{-1}5a_1^{-1}$ (0.02)
	^1E	26.84		$4a_1^{-1}2e^{-1}$ (0.02), $2e^{-2}$ (0.02)
			26.4	
	^1E	26.89		$2e^{-2}$ (0.01), $4a_1^{-1}2e^{-1}$ (0.02)
	^1E	28.99		$4a_1^{-1}2e^{-1}$ (0.01)
	$^1A_1$	29.14	30.4	$4a_1^{-2}$ (0.06), $5a_1^{-2}$ (0.03), $2e^{-2}$ (0.01)

IV. Summary

The present work illustrates that the multiple roots of nonlinear MRCC equations can be determined reliably. Reasonable agreements between the EIP/MRCC results and the experimental and previous correlated theoretical results for the diagram states of the Auger spectra of NH_3, PH_3, and HCl have been found. Critical aspects such as the correlated spacings of the diagram states in the third band of the spectrum of NH_3, the controversial position of the diagram state $^1\Sigma^+(5\sigma^{-2})$ in the spectrum of HCl, etc., have been discussed comparing the present findings with the earlier accurate calculations and experimental evidences. All calculated Auger satellitte roots obtained by using the cluster amplitudes $S_2^{(1,0)}$ corresponding to the alternative roots of the nonlinear MRCC equations at (1,0) valence rank level appear in the inner valence regions only which indicates the presence of strong correlation effects there. EIP/MRCC satellites for NH_3 agree well with the corresponding ADC(2) satellites indicating the worth of the present calculation. Theoretically found shake-up satellites by EIP/MRCC method provide a probable explanation for the broadening in the left part of the third band of the experimental spectrum of NH_3 observed by Camilloni et al. Unlike some earlier works (e.g., SDCI calculation on HCl or INDO (SCF) calculation on PH_3), the EIP/MRCC results for the diagram states in the inner valence regions of all the three molecules are consistently similar in their order of appearance which also reflects on the reliability of the present method. Discrepancies between the EIP/MRCC and the experimental values of the diagram states in the far left part of the inner valence region of each spectrum is presumably due to absence of the higher body cluster operators, $S_3^{(1,0)}$ and $S_3^{(2,0)}$, in the present calculation.

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