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A CSF-based multi-reference coupled pair approximation

III. An application to F_2, As_2 and As_2^+

Kiyoshi Tanaka[1], **Yuji Mochizuki**[2]

[1] Division of Natural Sciences, The University of Electro-Communications, 1-5-1, Chofugaoka, Chofu, Tokyo, 182, Japan
[2] Exploratory Research Laboratory, Fundamental Research Laboratories, NEC Corporation, Miyukigaoka 34, Tsukuba, Ibaraki, 305, Japan

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Abstract. Using the newly developed multi-reference coupled pair approximation program code, the adiabatic potential curves of the ground states of F_2, As_2 and As_2^+ were calculated. Computed spectroscopic constants of these molecules were found to be in good agreement with experimental values. The resulting binding energy of As_2 (3.86 eV) was compared with the experimental value of 3.99 eV [15] and the best multi-reference configuration interaction value (3.58 eV) reported previously by the present authors. The calculated first adiabatic ionization potential of As_2 (9.67 eV) was found to be in good agreement with the experimental result.

Key words: Multi-reference coupled pair approximation – Multi-reference single and double configuration interaction – Size consistency – Spectroscopic constants – Ionization potential

1 Introduction

Recent developments in computational quantum chemistry increasingly show the importance of the adequate treatment of electron correlation in the theory of the electronic structure of atoms and molecules [1, 2]. As a standard computational procedure for post-Hartree-Fock calculations, the configuration interaction (CI) method is well established in the field [3, 4]. It is, however, well known that any truncated CI, including multi-reference single and double excitation CI (MRSDCI), suffers from a principal difficulty, i.e. size inconsistency [5, 6]. Size inconsistency of truncated CI is caused by the lack of configurations of the higher excitations responsible for cancelling unlinked terms whose particle number dependence is incorrect. As a result, the quality of truncated CI calculations decreases as the number of correlating electrons increases. This inconsistency may lead to, for example, inappropriate or inaccurate potential energy surfaces, ionization potentials, and electron affinities.

The many body perturbation theory (MBPT) and the closely related coupled cluster method (CCM) constitute another predominant class of correlation method [5, 6]. Unlike truncated CI, both methods have the advantage of size consistency at each level of approximation [7–9]. The applicability of these methods to real systems, however, has been relatively limited to the case of a single reference function. There are many cases where the use of a set of multi-reference functions is required. It is noted that some attempts to incorporate multi-reference functions in MBPT/CCM have been made [10, 11].

Some trials to develop approximate size consistent theories where one can take advantage of the simple computational procedure of MRSDCI, for example averaged coupled pair functional (ACPF) [12a], quasi degenerate variation perturbation theory (QDVPT) [12b, 12c], and multi-reference coupled pair approximation (MRCPA) [12d, 12e] have been performed. Their many variations are reviewed by Szalay and Bartlett [12f].

MRCPA was proposed by one of the authors (K.T.) and co-workers and revealed the effectiveness of the method ([12d, 12e], which will subsequently be referred to as I and II, respectively). K.T. has developed a new computer program code for MRCPA which utilizes a symbolic energy expression file and a molecular integral file provided by Alchemy II [13] which can be used on workstations. Here, this method is applied to the adiabatic potential curves of the ground state of F_2 and As_2. The lowest ionization potential of As_2 is calculated. The major aims are to apply the method to the system which has a larger number of electrons than the systems considered in the previous papers (I and II), and to highlight the performance of this method.

2 Method

The formal theory of the present method is described in papers I and II. The equations to be solved are presented in this section. This scheme is fundamentally one of

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Correspondence to: K. Tanaka

multi-reference variants of coupled electron pair approximation [8, 9]. The present method, however, is based on the perturbation theory by partitioning the space spanned by configuration state functions (CSFs) into three parts: reference space, singly and doubly excited CSFs and higher excited CSFs. The unperturbed part of the electronic Hamiltonian matrix is a block diagonal of the three parts. The reference space block of the electronic Hamiltonian matrix was assumed to be diagonalized and the reference functions compose the zero-th order functions. The first-order perturbation theory led to a set of linear equations to determine the coefficients of the singly and doubly excited CSFs $\{C_{j\nu}^{(1)}\}$;

$$\sum_{j}^{SD}\{H_{\nu\nu}\delta_{ij}-H_{ij}\}C_{j\nu}^{(1)}=H_{i\nu}\ , \tag{1}$$

where H designates an electronic Hamiltonian, ν specifies one of the reference functions, and i and j run over the singly and doubly excited CSFs. This level of approximation is equivalent to the linearized version of CCM [11i, 11j]. The approximate third-order equation follows and is almost the same level as ACPF [12a] and an extension of QDVPT [12c];

$$\sum_{j}^{SD}\left\{(H_{\nu\nu}+\Delta_{\nu\nu}^{(i)})\delta_{ij}-H_{ij}\right\}\left(C_{j\nu}^{(1)}+\overline{C_{j\nu}^{(3)}}\right)=H_{i\nu}-\sum_{\mu\neq\nu}C_{i\mu}^{(1)}\left(\sum_{j}^{SD}H_{\mu j}C_{j\nu}^{(1)}\right)\ , \tag{2}$$

$$\Delta_{\nu\nu}^{(i)}=H_{\nu i}C_{i\nu}^{(1)}\ . \tag{3}$$

where $\Delta_{\nu\nu}$ is a contribution from the approximate remaining term after the cancellation of the higher terms by unlinked terms. The second term on the right-hand side of Eq. (2) represents the coupling between reference functions caused by the inclusion of electron correlation. This term was not taken into account in papers I and II. Although Eq. (2) provides an approximate size consistent wave function, the wave function gives additive separability of the total energy if the reference space guarantees proper separation of a molecule into two parts (for example, proper separation of a diatomic molecule into two atoms) which was shown in paper II and this remains even with the addition of the new term (the second term) on the right-hand side of Eq. (2).

Here, the second-order approximation is referred to as MRCPA (2) and the fourth-order approximation is referred to as MRCPA (4). Their energies were obtained by solving the following equation.

$$\sum_{\mu}\left[H_{\nu\nu}\delta_{\nu\mu}+\sum_{j}^{SD}H_{\nu j}C_{j\mu}\right]\alpha_{\mu}^{p}=E_{p}\alpha_{\nu}^{p}\ . \tag{4}$$

The second-order energy was obtained by using

$$C_{j\nu}=C_{j\nu}^{(1)} \tag{5}$$

and the fourth-order energy was obtained by using

$$C_{j\nu}=C_{j\nu}^{(1)}+\overline{C_{j\nu}^{(3)}}. \tag{6}$$

This mixing meant rotation in the reference space due to the inclusion of electron correlation. It may be significant near the avoided crossing point.

The concrete computational schemes applied to F_2, As_2 and As_2^+ will be described in the next section.

3 Calculations and results

Test calculations on BeH$_2$, N$_2$, H$_2$O, FH and O$_2$ are reported in papers I and II. Here we have carried out more extensive calculations on the systems with a larger number of electrons.

3.1 F_2

We carried out a calculation on the adiabatic potential curve of the electronic ground state $(^1\sum_g^+)$ of the F_2 molecule. We employed an extensive set of Slater type orbitals (STOs), (6*s*4*p*), given by Clementi and Roetty [14] and its outermost 2*p* STO with an exponent of 1.2657 was replaced by two STOs with exponents of 1.466 and 0.957. In addition to the set, two 3*d*-type STOs with exponents of 2.48360 and 3.9269 and a 4*f*-type STO with an exponent of 3.898 were augmented.

Initially we carried out a complete active space self-consistent field (CASSCF) calculation with active orbitals of $3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$. The CAS configurations are the following four configurations:

$$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^4 3\sigma_u^0\ , \tag{7a}$$

$$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2 3\sigma_u^2\ , \tag{7b}$$

$$\ldots 3\sigma_g^2 1\pi_u^2 1\pi_g^4 3\sigma_u^2\ , \tag{7c}$$

$$\ldots 3\sigma_g^0 1\pi_u^4 1\pi_g^4 3\sigma_u^2\ . \tag{7d}$$

Taking these as reference configurations, we carried out SDCI and CPA calculations with $1\sigma_g$ and $1\sigma_u$ kept frozen. In generating CSFs, the point group $C_{\infty V}$, subgroup of $D_{\infty h}$, was employed and the number of CSFs was 77 474.

We then checked how size consistency was retained by the CPA method. In order to do so, the same computational scheme was applied to the ground state of F atoms. As the CASSCF calculation with the previous four configurations leads to the two F atoms in the ground state configuration,

$$\ldots 2s^2 2p^5\ , \tag{8}$$

at the dissociation limit, we carried out the SDCI and CPA calculations of the ground state F atom by taking the ground state CSF, (8), as a reference function by keeping 1*s* as a frozen core. In Table 1, the total energy of two F atoms obtained by atomic calculation is compared with a molecular calculation with an internuclear separation of 50 a.u.. The energy difference by CPA of each level [CPA (2) or CPA (4)] resulted at only 0.02 eV. This shows that the degree of approximation by the CPA method does not decline as the number of electrons increases twofold. In contrast, the energy difference by the SDCI method amounted to 0.4 eV

Table 1. Comparison of total energies of two F atoms and F_2 at R = 50 a.u.

	Two F atoms	F_2 at R = 50 a.u.	Difference
CASSCF	−198.8224 a.u.	−198.8192 a.u.	3.2* 10^{-3} a.u.
SDCI	−199.2604 a.u.	−199.2454 a.u.	1.5* 10^{-2} a.u.
CPA(2)	−199.2779 a.u.	−199.2786 a.u.	7* 10^{-4} a.u.
CPA(4)	−199.2777 a.u.	−199.2785 a.u.	8* 10^{-4} a.u.

and this shows that the method suffers from size inconsistency.

The spectroscopic constants of F_2 were calculated by the four reference CSFs. In solving Eqs (1) and (2), the sets of vectors were obtained only for the lowest two states. Equation (4), therefore, reduces to a two-dimensional problem. It was found that the interaction between the two components was too small to rotate within the reference space. The results from the four reference functions are shown in Table 2. The degree of agreement with the experiment [15] using the CPA method is almost the same as with the CI method. Jankowski and co-workers [16] stressed the importance of the inclusion of 2π in the active space when calculating the ground state wave function. The CASSCF calculation taking $3\sigma_g$, $1\pi_u$, $1\pi_g$, $3\sigma_u$, $2\pi_u$, and $2\pi_g$ as active space was carried out and it was found that the following configurations were significant near the equilibrium inter-nuclear distance:

$$\ldots 3\sigma_g^1 1\pi_u^4 1\pi_g^3 3\sigma_u^1 2\pi_u^1 2\pi_g^0 \ , \tag{9a}$$

$$\ldots 3\sigma_g^1 1\pi_u^3 1\pi_g^4 3\sigma_u^1 2\pi_u^0 2\pi_g^1 \ , \tag{9b}$$

$$\ldots 3\sigma_g^2 1\pi_u^3 1\pi_g^3 3\sigma_u^0 2\pi_u^1 2\pi_g^1 \ , \tag{9c}$$

as well as the previously mentioned four reference configurations. The mixing of the first two augmenting configurations with the four reference configurations describes the left-right correlation between σ and π electrons which is not taken into account when using only the former four configurations. The seven configurations gave rise to 14 CSFs and we used them as reference functions near the equilibrium inter-nuclear distances. By keeping $1\sigma_g$ and $1\sigma_u$ as a frozen core, single and double excitations generated 709 370 CSFs. Only the lowest solution was utilized in obtaining the energy, which meant a one-dimensional problem in solving Eq. (4). By comparing the CI wave function, the lowest state reference function seemed to represent the leading part of the ground state approximately and higher state solutions suffered from a convergence problem. The total energies for SDCI, CPA(2), and CPA(4) at the respective equilibrium distance were −199.31272 a.u., −199.33865 a.u., and −199.33855 a.u.. The resulting spectroscopic constants are also included in Table 2 and are compared with the previous best values of Jankowski and co-workers [16], who utilized the MRSDCI scheme, and observed values [15]. The spectroscopic constants with the CPA method are in fairly good agreement with the observed values, especially the best binding energy which was obtained by 14RCPA.

Table 2. Spectroscopic constants of F_2

	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
Present			
4RSDCI	1.422	877	1.45
4RCPA(2)	1.419	899	1.49
4RCPA(4)	1.419	900	1.49
14RSDCI	1.418	911	1.83[a]
14RCPA(2)	1.423	896	1.63
14RCPA(4)	1.423	896	1.63
Other calculations			
Jankowski et al.[b]	1.420	–	1.59
Cartwright and Hay[c]	1.418	946	1.85
Obs.			
Huber and Herzberg[d]	1.412	917	1.66[e]

[a] 1.42 eV if the total energy of two F atoms is used for the dissociation limit

[b] Ref. [16]

[c] Ref. [17]

[d] Ref. [15]

[e] Including the zero-point energy correction

3.2 As_2 and As_2^+

We used one of the basis sets of segmented CGTOs used previously by the present authors [18] for As_2. This basis set is a set of CGTOs $[9s7p5d2f]$ designated as "$2d1f1f'/spd$" in the previous paper [18] and this is fundamentally composed of the set of GTOs given by Shäfer and co-workers [19] with augmenting functions. A detailed review of the theoretical calculations on this molecule is presented and results of extensive second-order (SO) CI calculations concerning $4s$ and $4p$ valence electrons are reported in the paper [18]. Here we add that the best binding energy even with a basis set which includes up to g-type function, $[8s6p4d2f1g]$ and a multi-reference variant of Davidson-type quadruple correction [9], was 3.58 eV, which is compared with the experimental value of 3.99 eV [15]. The sizeable difference between the calculated value and the experimental value remained. This suggests that the inclusion of electron correlation between the semi-valence ($3d$) shell and the valence ($4s, 4p$) shell is worthy of further investigation. Size consistency may be significant in such a case, because the number of electron pairs is increased more than two-fold. Although the basic set used in this work is slightly smaller than the best calculation and the binding energy was 3.40 eV (including quadruple correction) by the previous calculation with the present basis, spatial extension of one of the two basic f-type functions corresponds to that of the $4p$ region, whereas that of the other f-type function corresponds to the region of the average of the $4s$ and the $3d$ shell, so that the f-type functions are intended to be effective in accounting for electron correlation between the $3d$ shell and the valence ($4s, 4p$) shell. In obtaining the total wave functions, we used the natural orbitals (NOs) obtained from the wave function by the previous SOCI calculation. The number of CSFs amounts to the order of 10^6 even in the valence shell correlated SOCI calculation [18]. The size of the CSF set must be too large to carry out the calculation if we include CSFs reflecting correlation between the $3d$

shell and the valence ($4s, 4p$) shell electrons. We discarded some NOs of very small occupation number, thus suppressing the size of the CSF set to make the calculations tractable. Although the D_{2h} point group (sub-group of $D_{\infty h}$ point group) was employed to describe the wave function, the numbers of MOs of the irreducible representations by $D_{\infty h}$, σ_g, σ_u, π_u, π_g, δ_g, δ_u, ϕ_u, and ϕ_g, are 18, 18, 11, 11, 6, 6, 2, and 2, respectively, whereas the numbers of MOs in the original set are 23, 23, 14, 14, 7, 7, 2, and 2, respectively. In the correlation calculation, those MOs $1\sigma_g$–$5\sigma_g$, $1\sigma_u$–$5\sigma_u$, $1\pi_u$–$2\pi_u$, $1\pi_g$–$2\pi_g$ were kept frozen and they are described mainly by $1s$, $2s$, $2p$, $3s$, and $3p$ shells. A set of MOs mainly composed of semi-valence ($3d$) shell functions are $6\sigma_g$, $6\sigma_u$, $3\pi_u$, $3\pi_g$, $1\delta_g$, and $1\delta_u$. Those MOs of $7\sigma_g - 8\sigma_g$, $7\sigma_u - 8\sigma_u$, $4\pi_u$, and $4\pi_g$ were primarily led by $4s$ and $4p$ shells. Based on the results obtained by the previous calculation [18], we selected nine CSFs which are given by the following three configurations as reference functions for the near-equilibrium inter-nuclear distances;

$$\ldots 7\sigma_g^2 8\sigma_g^2 7\sigma_u^2 8\sigma_u^0 4\pi_u^4 4\pi_g^0\ , \tag{10a}$$

$$\ldots 7\sigma_g^2 8\sigma_g^2 7\sigma_u^2 8\sigma_u^0 4\pi_u^2 4\pi_g^2\ , \tag{10b}$$

$$\ldots 7\sigma_g^2 8\sigma_g^1 7\sigma_u^2 8\sigma_u^1 4\pi_u^3 4\pi_g^1\ , \tag{10c}$$

In addition to them, the following six configurations providing 11 CSFs were taken as reference configurations at the inter-nuclear distance of 100 a.u.:

$$\ldots 7\sigma_g^2 8\sigma_g^0 7\sigma_u^2 8\sigma_u^2 4\pi_u^2 4\pi_g^2\ , \tag{11a}$$

$$\ldots 7\sigma_g^2 8\sigma_g^1 7\sigma_u^2 8\sigma_u^1 4\pi_u^1 4\pi_g^3\ , \tag{11b}$$

$$\ldots 7\sigma_g^2 8\sigma_g^0 7\sigma_u^2 8\sigma_u^2 4\pi_u^0 4\pi_g^4\ , \tag{11c}$$

$$\ldots 7\sigma_g^2 8\sigma_g^0 7\sigma_u^2 8\sigma_u^2 4\pi_u^4 4\pi_g^0\ , \tag{11d}$$

$$\ldots 7\sigma_g^2 8\sigma_g^2 7\sigma_u^2 8\sigma_u^0 4\pi_u^0 4\pi_g^4\ , \tag{11e}$$

$$\ldots 7\sigma_g^2 8\sigma_g^0 7\sigma_u^2 8\sigma_u^2 4\pi_u^2 4\pi_g^2\ . \tag{11f}$$

The semi-valence MOs are doubly occupied in the reference functions. These 20 CSFs compose a CAS space within the active orbital space and guarantee proper dissociation of the wave function so that the total energy is additively separated into the two $^4S^0$ states of As atoms (paper II).

We applied the same occupational scheme to the lowest state, $^2\Pi_u$, of As_2^+. The reference configurations were as follows and 6 CSFs were generated from them:

$$\ldots 7\sigma_g^2 8\sigma_g^2 7\sigma_u^2 8\sigma_u^0 4\pi_u^3 4\pi_g^0\ , \tag{12a}$$

$$\ldots 7\sigma_g^2 8\sigma_g^2 7\sigma_u^2 8\sigma_u^0 4\pi_u^1 4\pi_g^2\ , \tag{12b}$$

$$\ldots 7\sigma_g^2 8\sigma_g^1 7\sigma_u^2 8\sigma_u^1 4\pi_u^2 4\pi_g^1\ . \tag{12c}$$

They are selected from CAS CSFs and the amplitudes of the remaining unselected CSFs are negligibly small near the equilibrium inter-nuclear distances.

The excited CSFs are generated by exciting electrons from the valence ($4s, 4p$) shell to take only intravalence shell correlation into account. The numbers of CSFs were 172 023 for 9 reference CSFs and 333 378 for 20 reference CSFs. When the computational scheme was further extended to include the correlation between semi-valence ($3d$ shell) and valence ($4s$, $4p$ shell) electrons, single excitations were allowed from both semi-valence and valence sets and double excitations were also allowed from semi-valence and valence sets except for simultaneous excitation from the semi-valence set. The total numbers of CSFs including intravalence correlation plus correlation between valence and semi-valence were 1 005 121 with 9 reference CSFs and 2 065 494 with 20 reference CSFs.

In order to check how the truncation in both NOs and CSFs affects the accuracy of the calculation, we carried out CI and CPA including only intravalence shell correlation with these reference functions and compared the results with those of the previous SOCI [18] for As_2. The total energy at an inter-nuclear distance of 100 a.u. and spectroscopic constants, D_e, R_e, and ω_e of the present CI calculation are compared with those of the previous SOCI calculation; they were −4468.44076 a.u., 3.49 eV, 2.13 Å, and 431 cm^{-1} by the present calculation and corresponding values are −4468.44318 a.u., 3.56 eV, 2.14 Å, and 416 cm^{-1} by the SOCI calculation. The truncation in both NOs and CSFs has only a small effect on the spectroscopic constants. We further carried out CPA calculations with 9 reference CSFs (20 reference CSFs at 100 a.u.). The corresponding values were −4468.46031 a.u., 3.70 eV, 2.14 Å, and 420 cm^{-1} by CPA(2) and −4468.46028 a.u., 3.69 eV, 2.14 Å, and 418 cm^{-1} by CPA(4). The binding energies by CPA(2) and CPA(4) were much better than those reported so far.

The computational scheme was further extended to include the correlation between semi-valence ($3d$ shell) and valence ($4s$, $4p$ shell) electrons. The computational results are listed in Table 3 together with the calculations which include only intravalence correlation and are compared with the previous computational results and experimental values. The CPA(4) scheme by intravalence plus inter semi-valence and valence correlation gives the

Table 3. Spectroscopic constants of As_2[a]

	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
Present			
Intravalence correlation			
9RSDCI	2.127	431	3.49[b]
9RCPA(2)	2.136	420	3.70[b]
9RCPA(4)	2.136	418	3.69[b]
Intravalence plus inter $3d$-valence correlation			
9RSDCI	2.109	441	3.61[b]
9RCPA(2)	2.116	430	3.86[b]
9RCPA(4)	2.116	431	3.86[b]
Other calculations			
Mochizuki and Tanaka[c]	2.133	417	3.58
Sakai et al.[d]	2.164	410	3.17
Obs.			
Huber and Herzberg[e]	2.102	429.6	3.99[f]

[a] A comparison with other results is made in Ref. [18]

[b] The total energy of the dissociation limit is obtained by the 20 reference CSFs (CAS CSFs)

[c] Ref. [18]; including quadruple correction by multi-reference variant of the Davidson scheme [20]

[d] Ref. [21]; a model potential treatment was used

[e] Ref. [15]

[f] Including the zero-point energy correction

best agreement with the experiment [15] among the results shown in the table. Inclusion of electron correlation between the 3*d* shell and the valence shell increases the binding energy by about 0.17 eV, decreases the equilibrium inter-nuclear distance by about 0.02 Å, and increases harmonic vibrational frequency by about 10 cm^{-1}. A comparison with other calculations was presented in our previous work [18]. Here we compare the present results with the best all electron calculation [18] and the best model potential calculation by Sakai and coworkers [21], which are included in Table 3. Our previous calculation was a SOCI calculation including only intravalence correlation using various extensive bases [18] whilst those shown in Table 3 are obtained by CGTOs of $[8s6p4d2f1g]$. The energy difference between their SOCI and the present 9RSCDI with valence shell correlation suggests that the binding energy by CPA including intervalence and semi-valence correlation may be improved by about 0.1 eV if *g*-type function is added to the basis set. In the study of Sakai and co-workers [21], only valence electrons are treated explicitly. By comparing their results with the present results and our previous results [18], it is found that 3*d* electrons should be taken into account explicitly if we employ model potential.

The ionization potential (IP) is another good way of checking for size consistency because of the difference in the number of electrons. The results are shown in Table 4 together with R_e and ω_e. Among the present calculations, val. SOCI means that correlation among valence electrons is taken into account and 9R calculations include intravalence plus intervalence and semi-valence electron correlation. The IPs by CPA lie between the experimental IP to $^2\Pi_{u3/2}$ and that to $^2\Pi_{u1/2}$. If we adopt experimental splitting, 0.174 eV, IP to the $^2\Pi_{u3/2}$ state is estimated to be 9.61 eV and that to the $^2\Pi_{u1/2}$ state is 9.79 eV by 9RCPA(4) and they are in excellent agreement with experimental results [22], 9.636 eV ($^2\Pi_{u3/2}$) and 9.810 eV ($^2\Pi_{u1/2}$). Agreement is much better than with the present CI and the other CI [22]. A comparison between val. SOCI and 9RSDCI indicates that the inclusion of intervalence-3*d* electron correlation increases IP by about 0.12 eV and is also significant in predicting IP of As_2.

Table 4. Spectroscopic constants of the lowest state, $^2\Pi_u$, of As_2^+ and ionization potential

	R_e (Å)	ω_e (cm^{-1})	IP (eV)
Present			
Val. SOCI	2.229	364	9.46
9RSDCI	2.206	382	9.58
9RCPA(2)	2.220	353	9.69
9RCPA(4)	2.220	354	9.67
Other calculation			
Wang et al.[a] $^2\Pi_{u3/2}$	2.230	347	9.32
$^2\Pi_{u1/2}$	2.231	347	9.50
Obs.			
Wang et al.[a] $^2\Pi_{u3/2}$	2.230	385	9.636
$^2\Pi_{u1/2}$	2.235	380	9.810

[a] Ref. [22]

4 Summary

A program code of the MRCPA theory was developed using Alchemy II. The program code was applied to F_2 and As_2 molecules. Through the computation on F_2, it was shown how size consistency is realized by the MRCPA method and how very good agreement of calculated spectroscopic constants with experimental data [15] was obtained by MRCPA. Theoretical prediction of the binding energy of As_2 was a very difficult problem. The present calculation showed that inclusion of electron correlation between the semi-valence (3*d*) shell and the valence $(4s, 4p)$ shell was significant together with intravalence correlation. Again very good spectroscopic constants of the molecule were obtained by the present method. The IP was also calculated and the best agreement with experimental data [22] was obtained by the present method.

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References

1. Löwdin P-O (1957) Adv Chem Phys 2:207
2. Wilson S (1984) Electron correlation in molecules. Clarendon Press, Oxford
3. Shavitt I (1977) In: Schaefer HF III (ed) Methods of electronic structure theory, vol 3. Plenum Press, New York, pp 189–276
4. Roos BO, Siegbahn PEM (1977) In: Schaefer HF III (ed) Methods of electronic structure theory, vol 3. Plenum Press, New York, pp 277–318
5. Bartlett RJ (1981) Annu Rev Phys Chem 32:359
6. Urban M, Cernusak I, Kellö V, Noga J (1987) In: Wilson S (ed) Methods in computational chemistry, vol 1. Plenum Press, New York, pp 117–239
7. Cizek J (1966) J Chem Phys 45:4256, (1969) Adv Chem Phys 14:35
8. Meyer W (1971) Int J Quantum Chem S5:341, (1972) J Chem Phys 58:1017, (1977) In: Schaefer HF III (ed) Methods of electronic structure theory, vol 3. Plenum Press, New York, pp 413–446
9. (a)Hurley AC (1976) Electron correlation in small molecules. Academic Press, New York; (b) Kutzelnigg W (1977) In: Schaefer HF III (ed) Methods of electronic structure theory, vol 3. Plenum Press, New York and London pp 129–188; (c) Ahlrichs R (1979) Comput Phys Commun 17:31
10. (a) Brandow BH (1967) Rev Mod Phys 39:771; (b) Lindgren I (1974) J Phys B (Lond) 7:2441
11. (a) Jeziorski B, Monkhorst HJ (1981) Phys Rev A24:1668; (b) Lindgren I (1978) Int J Quantum Chem S12:33; (c) Mukherjee D (1986) Chem Phys Letters 125:207; (d) Nakatsuji H (1985) J Chem Phys 83:713; (e) Lindgren I, Mukherjee D (1987) Phys Rep 151:93; (f) Meissner L, Jankowski K, Wasilewski J (1988) Int J Quantum Chem XXXIV:535; (g) Kutzelnigg W (1988) In:

Mukherjee D (ed) Aspects of many-body effects in molecules and extended systems. Lecture notes in Chemistry, vol 50. Springer, Berlin Heidelberg New York, pp 35–67; (h) Mukherjee D, Pal S (1989) Adv Quantum Chem 20:291; (i) Ladig WD, Bartlett RJ (1984) Chem Phys Lett 104:424; Ladig WD, Saxe P, Bartlett RJ (1987) J Chem Phys 86:887; (j) Tanaka K, Terashima H (1984) Chem Phys Lett 106:558

12. (a) Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413; (b) Cave RJ, Davidson ER (1988) J Chem Phys 89:6798, (1988) 88:5770; (c) Murray C, Racine SC, Davidson ER (1992) Int J Quantum Chem 42:273; (d) Tanaka K, Sakai T, Terashima H (1989) Theor Chim Acta 76:213, (I); (e) Sakai T, Tanaka K (1993) Theor Chim Acta 83:451 and references therein, (II); (f) Szalay P, Bartlett RJ (1995) J Chem Phys 103:3600
13. Lengthfield BH III (1980) J Chem Phys 73: 382; Lengthfield BH III, Liu B (1981) J Chem Phys 75:478; Liu B, Yoshimine M (1981) J Chem Phys 74:612
14. Clementi E, Roetty C (1974) Atomic data and nuclear data tables, 14:177
15. Huber KP, Herzberg G (1979) Constants of diatomic molecules, molecular spectra and molecular structure, vol IV. Van Nostrand, New York
16. Jankowski K, Becherer R, Scharf P, Schiffer H, Ahlrichs R (1985) J Chem Phys 82:1413
17. Cartwright DC, Hay PJ (1979) J Chem Phys 70:3191
18. Mochizuki Y, Tanaka K, and references therein (1997) Chem Phys Lett 274:264
19. Shäfer A, Horn H, Ahlrichs R (1992) J Chem Phys 97:2571
20. (a) Langhoff SR, Davidson ER (1974) Int J Quantum Chem VIII:61, Davidson ER, Silver DW (1977) Chem Phys Lett 52:403; (b) Buenker RJ, Shih S-K, Peyerimhoff SD (1979) Chem Phys 36:97
21. Sakai Y, Miyoshi E, Klobukowski M, Huzinaga S, J Chem Phys (in press)
22. Wang L-S, Lee YT, Shirley DA, Balasubramanian K, Feng P (1990) J Chem Phys 93:6310