



Study of isolated 1 : 1 Al³⁺.He complex using many-body perturbation theory : A multi-reference approach

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Abstract : Development and applications of many-body methods capable of reliable computation of potential energy curves (PEC) containing avoided curve-crossing zone remains a challenging area of activity in electronic structure theory till date. In this paper, we present the PEC of the ground state and the corresponding lowest charge transfer state of an isolated 1 : 1 Al³⁺.He complex, calculated using the third order effective valence shell Hamiltonian, H_v^{3rd} , method (a variant of quasi-degenerate multi-reference perturbation theory) and then analyze the aspect of avoided curve-crossing between these two states of the complex. The published theoretical data of this complex is very limited and to our knowledge no experimental data has been reported yet for the ground and excited electronic states of this complex. Thus, a comprehensive theoretical investigation of such a complex would be very useful to identify its structural properties. In our numerical analysis, a comparison of our findings is made with the results generated *via* other many-body methods whenever available. The results obtained from our method appear quite promising, implying the efficacy of H_v^{3rd} method to compute the energy surfaces (with degeneracy/quasi-degeneracy of varying degrees) over a wide range of geometries including the avoided curve-crossing zone. We further report the ground state spectroscopic constants of this complex obtained from the improved virtual orbital-complete active space configuration interaction (IVO-CASCI) based numerical gradient method. The spectroscopic constants predicted by the IVO-CASCI are in agreement with those determined from the state-of-the-art coupled cluster method.

Keywords : Al³⁺.He complex, avoided crossing, stability multi-reference perturbation method, geometry optimization

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1. Introduction

The fates of optical spectra and a host of dynamical processes pertaining to molecular

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systems having arbitrary level of complexity and generality are shaped to a large extent by the avoided crossings of the ionic and covalent potential energy curves. It is, however pertinent to mention that the curve-crossing phenomenon is not exclusive to molecular systems only, it rather extends even to systems as adsorbates on metal surfaces, typically involving an ionic interaction between the adsorbate and the adsorbent [1,2], thus taking into account the redox processes at metal surfaces and its obvious consequences to corrosion science. Thus, the importance of such studies not only encompasses the realm of traditional chemistry, it fans out to incorporate even the domains of physics and materials science. Noticeable among such phenomena are the spectroscopic abnormalities, pre-dissociation, quenching, energy transfer processes, ion-pair formation or recombination, chemi-ionization, collisional excitation, as well as the harpooning mechanism of chemical reactions. A molecular level understanding of the charge-transfer processes calls for real sophistication of the theoretical methodology to be developed and its consequent numerical implementation. Such a task could only be undertaken with a highly evolved insightful theoretical background and an algorithmic implementation of matching precision.

The theoretical and also experimental study of isolated 1 : 1 complexes between positively charged cation and ligand has pronounced importance in understanding of ionic bond and in the development of the Landau-Zener model for treating the curve-crossing phenomena. Such efforts have got recent impetus, and maintaining the spirit, we, in this article investigate the avoided potential energy curve (PEC) crossing of the ground state-singlet, $X^1\Sigma^+$ and the open-shell singlet, $A^1\Sigma^+$ (charge transfer state) states of isolated 1 : 1 $\text{Al}^{+3}.\text{He}$ complex using the third order effective valence shell Hamiltonian (H_V^{3rd}) method [3]. We recognize the fact that, although both the singlet and triplet charge transfer states, which originate due to the transfer of an electron from 1s orbital of He to 3s orbital of triply charged Al cation are possible for the complexes, only the singlet charge transfer state, $A^1\Sigma^+$ is involved in displaying the avoided crossing phenomenon with the ground state, $X^1\Sigma^+$. At this juncture it is relevant to highlight the fact that inspite of the growing interest in such compounds, the real knowledge about these are still in an infant stage. Thus, for a theoretical chemist it is quite arduous to come up with a prediction of the structural aspects of such type of complexes at the level of chemical accuracy. Among such studies, we mention the work of Wilson *et al* [4] on metal-He complexes, and the relatively recent article by Wright and Lee [5] on $\text{Al}^{+3}.\text{He}$ complex using various *ab initio* methods, concluding that the complex is kinetically stable.

The generation of smooth PECs containing various degrees of degeneracy is a crucial test case for multi-reference methods. The most stringent test of any MR-method for the computation of PEC is encountered in situations where the orbitals change very rapidly owing to very small geometrical distortions, as is frequently envisaged in the case of avoided curve-crossings. It is important to mention the fact

that the construction of the reference function is very crucial in order to scan the PEC over the wide range of geometries including curve-crossing region. The curve-crossings (conical intersections) are located at completely different internuclear distances if dynamical correlation is included, *vis-a-vis* the situation when it is based on a mean field description (say, MCSCF or CASSCF : complete active space self-consistent field). At the curve-crossing zone, the relative energies of the two states depend on which is chosen for orbital optimization, which can lead to root switching problems in an MCSCF (or CASSCF) calculation. Additionally, geometry optimization can cause root switching as well, if optimization passes through the conical intersection. To address this problem, it is possible to carry out a so-called 'state-averaged' MCSCF (or CASSCF) calculation. In a state-averaged calculation, the orbitals are variationally optimized not for any one state energy, but rather for the average of the two (or more than two, if a larger number of states are of interest). But it is important to recognize the fact that each state requires a different set of orbitals, meaning that one, *in principle*, should not use state-average calculations in a blanket manner. Rather, both states should be described in separate state selective calculations. This makes it hard to describe a smooth avoided crossing as the calculations cannot benefit from a joint diagonalization which would lead naturally to an avoided crossing as in (2×2) eigenvalue problem. A major objection of the state average calculation is that the quality of any one state's wave function is lower than what it would be were it to be the only state under consideration. On the other hand, a virtue of a state-averaged calculation is that all states are expressed using the same MOs, thereby ensuring orthogonality, which is critical if, say, transition dipoles between states are to be computed. A number of different weight factors were explored by various researchers for the state-averaged MCSCF (or CASSCF), and there is considerable sensitivity exhibited in the convergence of the MCSCF (or CASSCF) calculation to the weights of the states used. Thus, state average MCSCF (or CASSCF) calculations are very laborious in the sense that to reproduce the proper pattern of the avoided crossing a plethora of numerical analyses are needed regarding weight factors of the two states involved. To overcome these 'objections', one can use a very large CAS.

The CAS-based perturbative methods which are used as rigorous models capable of reliable computations of PEC for systems of arbitrary complexity and generality are H_v [3], MRMP [6], MCQDPT [7], CASPT2 [8], MRMP using APSG [9], CIPSI [10], and so on. The various CAS-based perturbative methods can also differ in their choice of unperturbed Hamiltonian apart from the mode of representing the reference function in the context of relaxed or unrelaxed coefficients. At this point, it is pertinent to mention the work of Mukherjee and co-workers [11]. The SS-MRCC method [12] of Mukherjee and co-workers allows transparent simplification *via* truncation of the working equations, leading to various perturbative methods (termed as SS-MRPT [11]) of practical utility. The well known effective valence shell Hamiltonian (H_v) method developed by Freed and

co-workers [3] is based on quasi-degenerate many-body perturbation theory. The efficiency and accuracy of the H_v method has already been tested and demonstrated with numerous examples, and several studies on the convergence properties explain why these successes have been achieved. The effective valence shell Hamiltonian, H_v method is obtained by projecting the full Hamiltonian onto a valence space that is spanned by a pre-chosen set of valence orbitals. The projection can be accomplished with the aid of quasi degenerate many-body perturbation theory. We will discuss the detailed theoretical aspect of this method in the next section. The MCQDPT approach starting from a MCSCF (or CASSCF) wave function is another effective method for recovering dynamic correlation. It is computationally efficient when compared with the alternative of MRCI method as is the case for H_v method. However, the H_v method is computationally less expensive than the MCQDPT method, since it (i) does not require iterations beyond those in the initial SCF calculation, (ii) is free from convergence difficulties which arise due to the intruder effect with increasing size of the CAS in CASSCF calculations. The H_v approach generates both singly and doubly excited states with accuracy comparable to CASSCF treatments as it contains higher order excitations in addition to the singly and doubly excited configurations in the CAS. Not only that, the latter contrasts with the CIS method which cannot treat doubly excited states. Not only that, the IVO-CASCI scheme differs from the traditional CI approach in the evaluation of orbitals and orbital energies. The traditional CI method determines both the occupied and unoccupied orbitals and their orbital energies using a single Fock operator in which the unoccupied orbitals describe the motion of an electron in the field of N other electrons. Consequently, the virtual orbitals are, at best, more appropriate for describing negative ion states than the low lying excited states of interest. The H_v method obtains the unoccupied orbitals and their energies from a set of V^{N-1} potential Fock operators in order to optimize the CASCI predictions of low lying electronic states and thereby to minimize the higher order perturbative corrections. In this paper, we mainly concentrate on the applicability of the third order H_v method to compute the PEC involving avoided curve-crossing of a very interesting and challenging $\text{Al}^{+3}.\text{He}$ complex. To establish the effectiveness of the H_v method, we have also generated the same using MCQDPT method [7] for comparison.

The determination of the location of stationary points on PECs (and hence the determination of equilibrium and transition state structures) through geometry optimization using efficient techniques is a very challenging task for any theoretical chemist. The theoretical determination of optimized molecular geometries and vibrational frequencies requires the computation of derivatives of the total energy with respect to all internal coordinates. Ideally, energy gradient should be determined analytically since numerical energy derivative scheme is computationally expensive owing to the fact that the energy is computed twice along each of the totally symmetric modes (for the backward and forward displacements). The gradient technique for the calculation of molecular properties had been in vogue for at least a couple of decades. Needless to highlight is the fact

that such methods have been exploited mostly in the realm of single reference context. However, the adoption of the same strategy within the periphery of a genuinely MR method is still in the stage of infancy. Thus, it would serve as a challenge for a theoretical chemist to develop a truly MR based analytic derivative method for the property calculation in general. We, in this article, embark on such a sojourn and exploit our newly developed numerical derivative based IVO-CASCI (developed by Chaudhuri *et al* [13]) method to compute the equilibrium bond length and vibrational frequencies, and other spectroscopic properties *via* geometry optimization. To test the quality of the perturbed wave-function generated *via* IVO-CASCI method, we study the spectroscopic parameters of the Al⁺³.He complex *via* numerical gradient technique [13]. The Al⁺³.He system is sufficiently complex for benchmarking the ability of the numerical gradient based IVO-CASCI method for describing the ground state geometry and vibrational frequencies. We want to emphasize the fact that the IVO-CASCI method has wide applicability in situations such as (i) calculations of atomic spectra, (ii) computation of PEC and electronic spectra starting from simple di-atomic to extended molecular systems.

We are now in a position to discuss the organization of our paper. The organization of the paper is as follows. In Section 2, we will describe the theoretical development of the H_v method. The discussion on numerical analysis of various results are presented in the Section 3. The last section consists of our summarizing remarks.

2. Theoretical considerations

A. Generation of Improved Virtual Orbitals :

One portion of the CASSCF procedure effectively involves a CASCI computation using orbitals optimized for a single state or for some weighted average of several states. A CI computation of dimension D is well known to provide rigorous upper bounds to the energies of the D lowest electronic states [14] but, of course, accurate bounds are expected only for the lowest few of these states, which, fortunately, are generally the states of interest. However, the use of orbitals optimized for one (or for the average of a few) states generally yields a poor representation of the other states, and this feature is partially responsible for the poor convergence of the CASSCF procedure as the dimension of the CAS grows. Our alternative approach involves directly choosing orbitals that simultaneously provide a good representation for several of the lowest lying electronic states. This procedure is followed in H_v computations in which the CAS orbitals are defined as comprising the highest occupied orbitals (perhaps, only for certain symmetries) in the SCF approximation to the ground (or a low lying) state and a set of the lowest lying IVO orbitals constructed from the remaining unoccupied space in the basis set. This approach is designed to maximize the accuracy of the first order H_v approximation, which is equivalent to a CASCI, for the low lying electronic states in order to minimize the required perturbative corrections [15]. Earlier H_v computations

used a computationally complex sequence of SCF computations to obtain the IVOs, but more recently they employ a simple direct method for generating the IVOs for several common situations [16]. The significant improvement in computational efficiency for determining the IVOs is one of the important features contributing to the packageability of the IVO-CASCI method [17] and its use for geometry optimization [13].

Since the basic philosophy of generating the IVOs is the same for both restricted and unrestricted HF orbitals, we only present the restricted HF case, which is used herein. When the ground state of the system is a closed shell, we begin with the Hartree-Fock (HF) molecular orbitals (MOs) for the ground state wave-function, $\bar{\psi}_0 = \mathcal{A}[\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 \cdots \phi_n\bar{\phi}_n]$ where \mathcal{A} is the antisymmetrizer. Let the indices i, j, k, \dots refer to the occupied HF MOs $\{\phi_j\}$ and u, v, w, \dots to unoccupied HF MOs. All the HF MOs are determined by diagonalizing the one electron Hartree-Fock operator 1F ,

$${}^1F_{lm} = \left\langle \phi_l \left| H + \sum_{k=1}^{\text{occ}} (2J_k - K_k) \right| \phi_m \right\rangle = \delta_{lm} \epsilon_l, \quad (1)$$

where l and m designate any (occupied or unoccupied) HF MO and ϵ_l is the HF orbital energy. The operator H is the one-electron portion of the Hamiltonian, and J_k and K_k are Coulomb and exchange operators, respectively, for the occupied orbital ϕ_k .

An excited state HF computation would provide a new set $\{\chi\}$ of MOs that produce the lowest possible energies for the low lying singly excited $\bar{\psi}_{\alpha \rightarrow \mu}$ state,

$$\bar{\psi}(\alpha \rightarrow \mu) = \mathcal{A} \left[\chi_1\bar{\chi}_1\chi_2\bar{\chi}_2 \cdots (\chi_\alpha\bar{\chi}_\mu \pm \chi_\mu\bar{\chi}_\alpha) \cdots \chi_n\bar{\chi}_n \right], \quad (2)$$

corresponding to an excitation of an electron from the orbital χ_α to χ_μ , where the + and - signs correspond to triplet and singlet states, respectively. The new MOs, $\{\chi_\alpha\}$ and $\{\chi_\mu\}$ may be expressed as a linear combination of the ground state MOs $\{\phi_i, \phi_u\}$. If, however, the orbitals are restricted such that the $\{\chi_\alpha\}$ are linear combinations of only the occupied ground state MOs $\{\phi_\alpha\}$ and the $\{\chi_\mu\}$ are expanded only in terms of the unoccupied $\{\phi_u\}$,

$$\chi_\alpha = \sum_{i=1}^{\text{occ}} a_{\alpha i} \phi_i; \quad \chi_\mu = \sum_{u=1}^{\text{unocc}} c_{\mu u} \phi_u, \quad (3)$$

then the new orbital set $\{\chi_\alpha, \chi_\mu\}$ not only leaves the ground state wave-function unchanged but also ensures the orthogonality and applicability of Brillouin's theorem between the HF ground state and the $\bar{\psi}_{\alpha \rightarrow \mu}$ excited states. In addition, this choice also benefits from using a common set of MOs for the ground and excited states, a choice which simplifies the computation of oscillator strengths, etc. However, we avoid the computationally laborious re-optimization of the occupied orbitals by setting $\{\chi_\alpha\} \equiv \{\phi_\alpha\}$, i.e., by choosing $a_{\alpha i} = \delta_{\alpha i}$, thereby simplifying enormously the procedure for generating the IVOs. Hence, the coupled equations determining the coefficients $a_{\alpha i}$ and $c_{\mu u}$ reduce

to a single eigenvalue equation of the form $F'C = CI$, where the operator F' is given by

$$F'_{vw} = {}^1F_{vw} + A_{vw}^\alpha, \quad (4)$$

where 1F is the ground state Fock operator and the additional term A_{vw}^α accounts for the excitation of an electron out of orbital ϕ_α ,

$$A_{vw}^\alpha = \langle \chi_v | -J_\alpha + K_\alpha \pm K_\alpha | \chi_w \rangle. \quad (5)$$

The minus sign in eqs. (2, 5) applies for ${}^3\Psi_{\alpha \rightarrow \mu}$ a triplet state, while the plus sign is for the singlet ${}^1\Psi_{\alpha \rightarrow \mu}$ state [18-20]. The corresponding transition energy is

$${}^{1,3}\Delta E(\alpha \rightarrow \mu) = E_0 + \gamma_\mu - {}^1F_{\alpha\alpha}, \quad (6)$$

where E_0 is the HF ground state energy and γ_μ is the eigenvalue of $PC = CI$ for the μ -th orbital.

B. The effective valence shell Hamiltonian (H_v) method :

As in conventional many-body perturbation theory, the H_v method [3] begins with the decomposition of the exact Hamiltonian H into the zeroth order Hamiltonian H^0 and the perturbation V . The zeroth order Hamiltonian H_0 is assumed to yield a complete set of eigenvectors $\{\phi_i\}$ with eigenvalues $E_i^{(0)}$. The full space in which H operates is then partitioned into a small reference space with the projector

$$P = \sum_{i=1}^d |p_i\rangle \langle p_i|, \quad (7)$$

and its orthogonal compliment

$$Q = 1 - P = \sum_{j=d+1}^{\infty} |q_j\rangle \langle q_j|, \quad (8)$$

where the sets $\{p_i\}$ and $\{q_j\}$ span the reference and complimentary spaces, respectively, and d is the dimension of the reference space. The reference space functions $|\Psi_m^0\rangle$ are the projections on the reference space of the exact eigenfunctions $|\Psi_k\rangle$,

$$|\Psi_k^0\rangle = P |\Psi_k\rangle \quad (9)$$

and the wave operator Ω can be used to regenerate the exact eigenfunctions,

$$|\Psi_l\rangle = \Omega |\Psi_l^0\rangle. \quad (10)$$

Using the projectors P and Q , the full Schrödinger equation ($H|\Psi_m\rangle = E_m|\Psi_m\rangle$) can be transformed into the effective Schrödinger equation,

$$H_{\text{eff}} |\Psi_m^0\rangle = E_m |\Psi_m^0\rangle, \quad (11)$$

where E_m are the corresponding exact energies, and $H_{\text{eff}} = PH\Omega P$. The effective operator H_{eff} through third order is given by

$$H_v = PHP + \frac{1}{2} [V_{\text{eff}}^{(2)} + V_{\text{eff}}^{(3)} + h.c.] , \quad (12)$$

in which *h.c.* designates the Hermitian conjugate of the preceding terms in square brackets.

Here, the operators $V_{\text{eff}}^{(2)}$ and $V_{\text{eff}}^{(3)}$ are defined as

$$V_{\text{eff}}^{(2)} = PV \frac{Q}{E_0^P - H_0^Q} VP, \quad (13)$$

$$V_{\text{eff}}^{(3)} = PV \frac{Q}{E_0^P - H_0^Q} V \frac{Q}{E_0^P - H_0^Q} VP - PV \frac{Q}{(E_0^P - H_0^Q)^2} VPVP. \quad (14)$$

where E_0^P is the zeroth order energy (see below) of the *P*-space states. Apart from the choice of reference (*P*) space, the only variability in all multi-reference many-body perturbative theories (MR-MBPT) lies in the choice of orbitals, orbital energies, and the definition of the zeroth order Hamiltonian H_0 since the perturbation approximation is completely determined by these choices. The zeroth order Hamiltonian is, generally, prescribed as a sum of one-electron operators,

$$H_0(i) = \sum_c |\phi_c\rangle \epsilon_c \langle \phi_c| + \sum_v |\phi_v\rangle \epsilon_v \langle \phi_v| + \sum_e |\phi_e\rangle \epsilon_e \langle \phi_e| , \quad (15)$$

in terms of the core (*c*), valence (*v*) and excited (*e*) orbitals and their corresponding orbital energies. Unlike traditional MR-MBPT, the zeroth order Hamiltonian H_0 in the H_v method is defined as

$$H_0(i) = \sum_c |\phi_c\rangle \epsilon_c \langle \phi_c| + \sum_v |\phi_v\rangle \bar{\epsilon}_v \langle \phi_v| + \sum_e |\phi_e\rangle \epsilon_e \langle \phi_e| , \quad (16)$$

to improve the perturbative convergence [21]. The average valence orbital energy $\bar{\epsilon}_v$ in eq. (16) is obtained from the original set of valence orbital energies by the democratic averaging,

$$\bar{\epsilon}_v = \frac{\sum_i^{N_v} \epsilon_i}{N_v} , \quad (17)$$

with N_v being the number of valence orbitals ϕ_v spanning the complete active *P* space (CAS). The valence orbitals ϕ_v that are unoccupied in an SCF approximation for the ground state are determined, along with their orbital energies ϵ_v , using improved virtual orbitals (IVOs). The first order approximation, the *PHP* term in eq. (12) provides the IVO-CASCI method, which has been shown to provide comparable accuracy to the CASSCF approximation without the need for iterations beyond the initial SCF

approximation (see Ref. [16]).

3. Results and discussion

In this section, performance of the H_v method is assessed in the case of $Al^{+3}.He$ complex. The numerical application of H_v method consists of two parts : (i) computation of PEC using third order H_v method and (ii) calculations of spectroscopic parameters via geometry optimization technique using numerically oriented gradient based IVO-CASCI method which is a first order approximation within the H_v method.

We will present the potential energy curve of the two lowest states showing avoided crossing in an 1 : 1 isolated complex $Al^{+3}.He$ using H_v method. To get a better feeling of the potentiality our method, we will also incorporate the results of high level *ab initio* calculations : such as MCQDPT and CR-CCSD(T) [24]. The CR-CCSD method and its different variants are very powerful tools for computing and also predicting the structures, energetics, and many other properties of atomic and molecular systems of arbitrary complexity and hence, can be used as a benchmark. However, it is worth mentioning that the CC-method is computationally more demanding than the perturbative MR method. In spite of this, since the experimental results are not available for this system, here we have used CR-CCSD(T) results as reference for comparative study. Since the systems under investigation are highly positively charged species, it is necessary to use the *correlation consistent augmented* basis sets to describe the core region properly. For this reason, in our numerical implementation we have employed aug-ccpVXZ level of basis sets. In our study, the ground state geometrical parameters of $Al^{+3}.He$ are computed using aug-cc-pVTZ basis sets whereas aug-cc-pVQZ basis sets [25] are used for state energy calculation, since the larger basis sets are the most reliable for the study of PEC (potential energy curve). Although He is a neutral species, we have used the same corresponding basis sets in each case.

As we have already mentioned, the ground $X^1\Sigma^+$ state PEC of the complex possesses quasi-degeneracy at some points and there is a potential avoided curve-crossing at another point with the open-shell singlet, $A^1\Sigma^+$ state. The orbitals change very rapidly as a function of the minor geometrical distortion as happens in the region of curve-crossing. From the theoretical point of view, this complex thus poses a serious challenge to any theory where both dynamical and non-dynamical correlations are important in varying degrees along the PEC. Consequently, to describe the PEC of the complex properly, multi-reference method instead of a single reference one is a more judicious choice. A two step approach has been used in our calculations : (i) the most important non-dynamical correlations are treated at the CASSCF level and (ii) dynamical correlation effects are taken into account using the H_v^{3rd} method based on CASSCF zeroth-order reference function. In our computations, the complete active space (CAS) used for the geometry optimization is constructed from 8 active electrons (1s and 2s orbital of metal atom is kept frozen) and 10 active MOs (4 of a_1 symmetry, 3 of b_1

symmetry, and 3 of b_2 symmetry).

The energies for H_V^{3rd} ground state $X^1\Sigma^+$ and the excited $A^1\Sigma^+$ state as a function of Al-He internuclear distance are depicted in Figures 1 and 2. For comparison, we have plotted the results of MCQDPT and CR-CCSD(T) methods in Figures 1 and 2 respectively. Figure 1 demonstrates the fact that H_V^{3rd} method, just like the MCQDPT method, is quite effective to scan the PEC of the complex over the various geometries

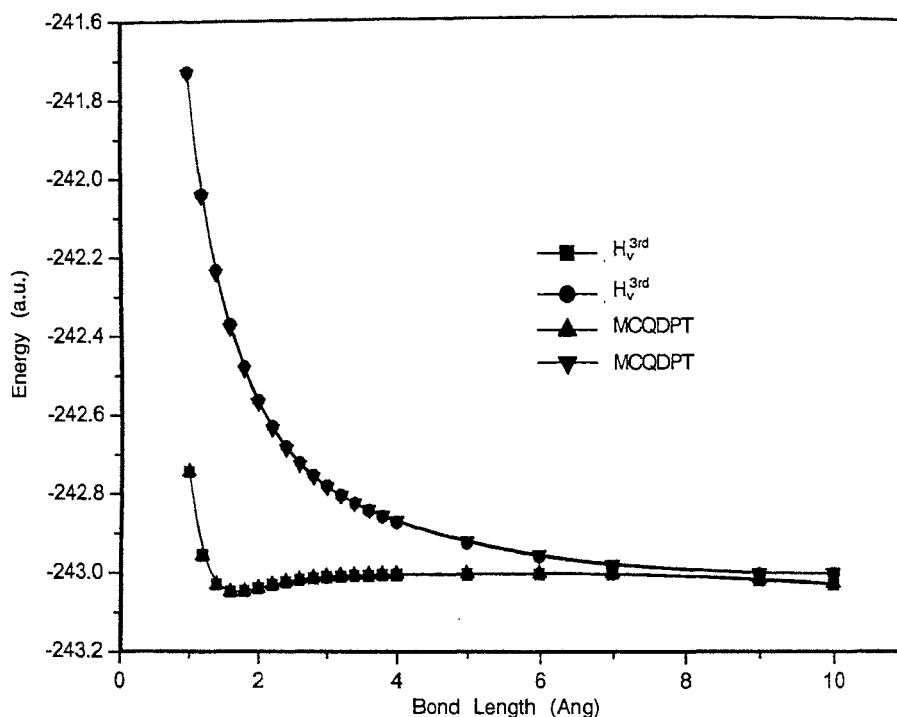


Figure 1. PECs for the two lowest singlet sigma states of $Al^3\cdot He$ complex including the region of their avoided crossing.

including the zone of avoided crossing. At this juncture, we might reiterate that the H_V method is computationally less demanding than the MCQDPT method, a fact already discussed in the Introduction section. From the graphical representation (Figure 2), it is also evident that the performance of the H_V^{3rd} method to compute the PEC of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states is consistent with the high-level ab initio CR-CCSD(T) method. To get a clear picture of the performance of H_V^{3rd} method towards generating the region of avoided curve-crossing, we have also presented an expanded view of the crossing zone for the results of H_V^{3rd} method in Figure 3. It is important to mention the fact that the extent of mixing of the two eigenstates, ground state $X^1\Sigma^+$ and the excited $A^1\Sigma^+$ state, involved in curve-crossing is not quite strong which is evident from the sharp nature of the avoided crossing presented in the Figure 3. It is also clear from the depth of the PEC (generated using H_V^{3rd} , MCQDPT and CR-CCSD(T) methods) at equilibrium

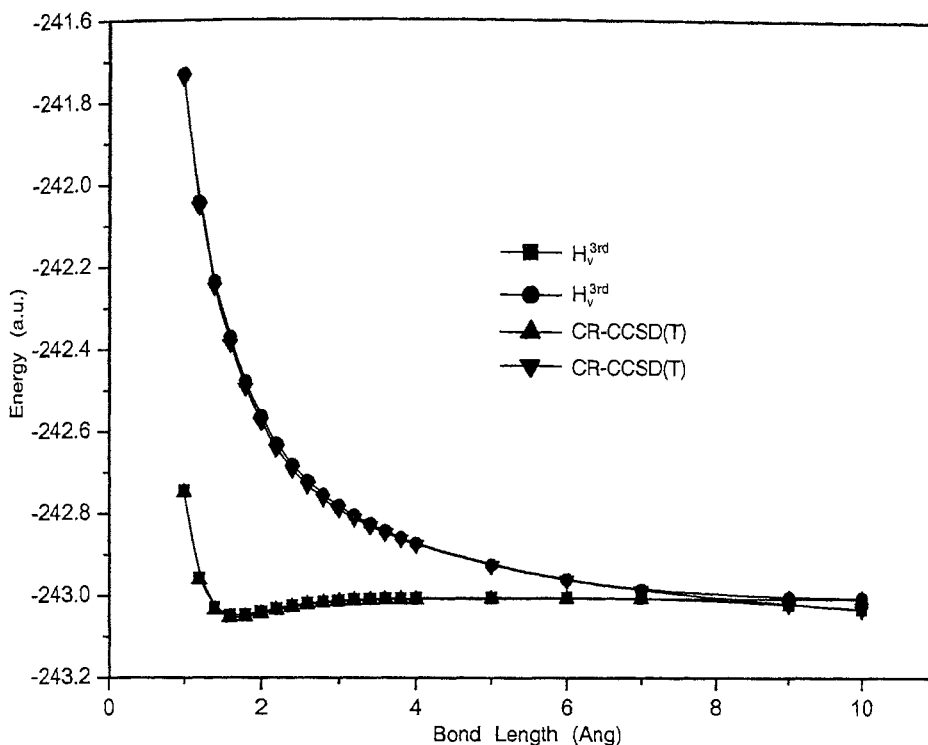


Figure 2. PECs for the two lowest singlet sigma states of $\text{Al}^{+3}.\text{He}$ complex including the region of their avoided crossing.

position of the ground state that the 1 : 1 isolated $\text{Al}^{+3}.\text{He}$ complex is expected to be strongly bound in nature (*i.e.* kinetically stable). Wright and Lee [5] also found that the binding for the ground state of $\text{Al}^{+3}.\text{He}$ complex exhibits a deep minimum in the potential energy curve.

Since various variants of H_v method are quite useful to compute the energetics recovering both the non-dynamical and dynamical correlation in an effective and balanced manner for different nuclear configuration over entire region of PEC of notoriously difficult systems such as $\text{Al}^{+3}.\text{He}$ complex, the H_v method is expected to provide reasonable results for various spectroscopic constants using numerical gradient scheme. The molecular geometries and vibrational frequencies are essential ingredients in finding the reaction paths and in identifying the end products of a chemical reaction, hence, we have also computed various spectroscopic constants using the geometry optimization technique. This calculation will not only establish the applicability of the H_v method to compute the spectroscopic constants but also present the generality of the method. Here, we apply the IVO-CASCI geometry optimization method using numerical derivatives in order to compute the bond length, vibrational frequencies and other spectroscopic constants of the 1 : 1 isolated $\text{Al}^{+3}.\text{He}$ complex which is a sufficiently difficult system to assess the potentiality of the method. The geometry

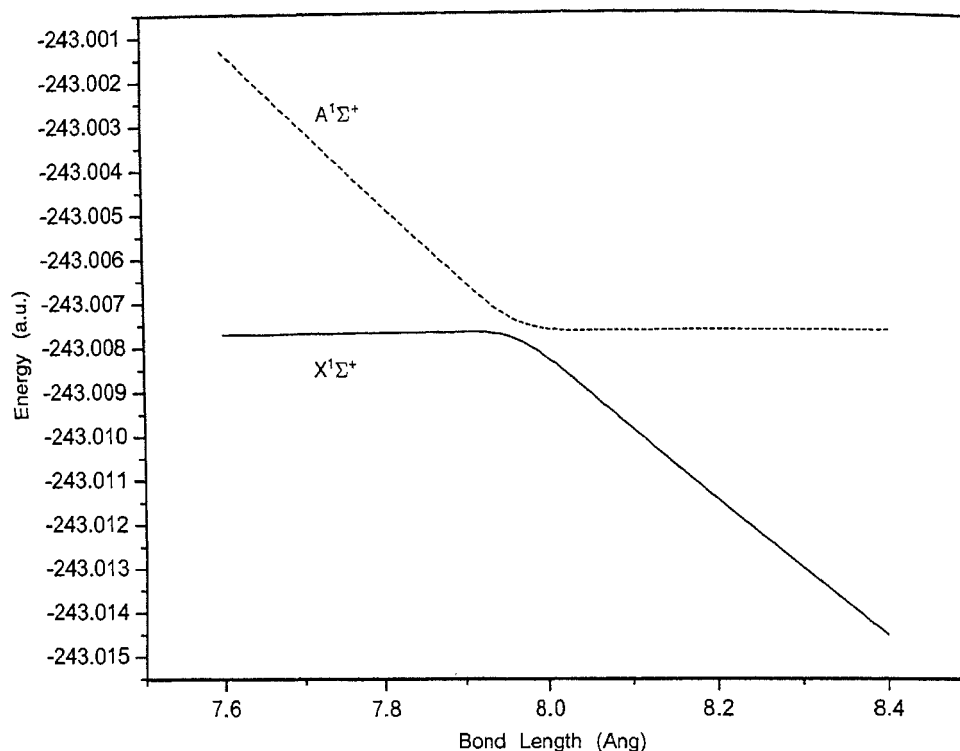


Figure 3. Expanded view of PECs of $\text{Al}^{+3}.\text{He}$ complex using H_V^{3rd} method in the vicinity of avoided crossing zone.

optimization is accomplished by interfacing the IVO-CASCI method into the GAMESS program [22] which also supports numerical gradient calculations for the CCSD scheme [23]. The CCSD method provides a very accurate estimate of the equilibrium bond length for the ground state. For comparative study, we have also quoted the results of geometry optimization generated *via* CASSCF-based response method. The CASSCF optimized geometries and vibrational frequencies are computed using the Dalton package [26]. We emphasize that the CASSCF scheme computes energy derivatives analytically. We highlight the fact that the IVO-CASCI method presented in this article (which has the same range of applicability as CASSCF treatments) is not susceptible to the convergence problems that often plague the traditional CASSCF approach. For comparison, coupled cluster calculations are also included in our numerical analysis of the gradient based IVO-CASCI geometry optimization of the $\text{Al}^{+3}.\text{He}$ complex. The computer time needed for the IVO-CASCI method (and also CASSCF) for geometry optimization is at least an order of magnitude less than the various coupled cluster approaches. If the computational efficacy of the theory is successfully established for a molecular system of arbitrary complexity and generality, then one can use the gradient-based IVO-CASCI method as a handy tool for geometry optimization.

In Table 1 we have presented the various spectroscopic constants using the

Table 1. Spectroscopic constants of Al⁺³.He complex using aug-ccpVQZ basis [Entries within parentheses are obtained from aug-cc-pVDZ basis].

	CASSCF	IVO-CASCI	CCSD	CCSD(T) ^a
$R/\text{\AA}$	1.678 (1.745)	1.673 (1.735)	1.672(1.747)	1.663
ω_e/cm^{-1}	811 (731)	815 (746)	815(735)	839.8
D_e/cm^{-1}	10876	10888	10859	10715
B_e/cm^{-1}	1.717 (1.587)	1.726 (1.606)	1.729(1.584)	1.757

numerical gradient-based first-order H_v method (IVO-CASCI) and CCSD methods along with results of other available methods. In the table we have reported the values using aug-ccpVDZ and aug-ccpVQZ basis sets to indicate the variation due to basis set extension. From the values of various spectroscopic parameters presented in Table 1, we can say that the results obtained from the two basis sets using IVO-CASCI and CCSD method are very close. It is important to mention the fact that the results generated using larger basis sets are more reliable to compute the spectroscopic constants from the point of view of basis set saturation. The spectroscopic constants generated *via* numerical gradient-based IVO-CASCI method mimic very nicely the results of the full-blown CCSD(T) methods (see Ref. [5]). Wide applications over the last decade or so have established the ability of the CCSD(T) [27] method to display results with a high level of accuracy. From the table it is also evident that the binding energy and vibrational frequency are both quite large which also establishes the fact that the Al⁺³.He complex is expected to be a kinetically stable one inspite of the fact that it is not possible to isolate the complex experimentally. The high quality results demonstrate the fact that the IVO-CASCI-based gradient technique can serve as a good theoretical model for geometry optimization along with the corresponding calculation of various spectroscopic parameters.

4. Conclusion

In this paper, we have investigated the various structural properties of the isolated 1 : 1 Al⁺³.He complex which has not been identified experimentally till date. The system is sufficiently complex for judging the ability and generality of the MR methods for describing the energetics, geometry and vibrational frequencies. We have calculated the PECs of the ground state-singlet, $X^1\Sigma^+$ and the open-shell singlet, $A^1\Sigma^+$ including avoided curve-crossing region of isolated 1 : 1 Al⁺³.He complex (using very large basis sets) generated *via* the H_v^{3rd} method. For a comparative study relating to the applicability and generality of the method, we have also compared the results generated *via* H_v^{3rd} method with other high level *ab initio* methods : MCQDPT and CR-CCSD(T). From this comparative study, we notice that the H_v^{3rd} method (which treat the non-dynamical and dynamical correlation effects in a correct and balanced manner) is not only very promising for description of the PECs of the ground and the singlet open-shell excited $A^1\Sigma^+$ states of the isolated 1 : 1 Al⁺³.He complex but is also effective

for the correct description of the region of avoided curve-crossing. The promising quality of the PEC of the complex prompted us to study the spectroscopic parameters of the complex. The numerically oriented energy gradient based IVO-CASCI method is used to compute the vibrational frequency for the ground state of the complex *via* the geometry optimization scheme. We have also been able to demonstrate the fact that the spectroscopic results obtained from the IVO-CASCI-based numerical gradient are in close proximity to the corresponding results of other standard approaches such as CCSD(T) method. The accuracy of the results of H_v^{3rd} and numerical gradient version of the IVO-CASCI (first order H_v) methods with respect to other standard methods (such as CC, MCQDPT and so on) for the $Al^{+3}.He$ system which is sufficiently complex in nature, explicitly demonstrates the efficacy of the H_v methods. Although it is not possible to isolate the $Al^{+3}.He$ complex experimentally from the numerical analysis of H_v^{3rd} and gradient based IVO-CASCI methods (along with other highly sophisticated *ab initio* methods), it is quite evident that the complex is kinetically stable in nature. The numerical gradient based IVO-CASCI is not free from objection in spite of the good quality of results since the numerical gradient procedure is computationally expensive. To overcome this difficulty, it would be very useful to develop the analytic derivative formulation of the IVO-CASCI method, an issue which we have already started working on. We conclude this article with the hope that the experimentalists would soon isolate such a chemically interesting and kinetically stable complex.

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