Vol 17 No 6, June 2008
1674-1056/2008/17(06)/2040-08
Chinese Physics B
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The splitting of low-lying or low excited states for hydride molecules (cations) of the third period under spin-orbit coupling*

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(Received 22 September 2007; revised manuscript received 19 October 2007)

This paper reports that the splitting of potential energy curves for the low-lying or low excited states for hydride molecules (cations) (MgH, AlH^+, SiH, PH^+, SH,ClH^+) of the third period under Spin-Orbit Coupling has been calculated by using the Spin-Orbit Multi-Configuration Quasi-Degenerate Perturbation Theory (SO-MCQDPT) method. Then, spectroscopic constants of the split states have been derived from the Murrell–Sorbie function. The calculated dissociation energies for the spectrum branch terms have been given, respectively. The spectroscopic constants and dissociation energies for the spectrum branch terms are given for the first time in this paper.

Keywords: SOC, hydrides, spectroscopic constants, SO-MCQDPT method
PACC: 3150, 7170E

1. Introduction

Spin–orbit coupling (SOC)[1,2] is a kind of magnetic effect, and in fact, a relativistic effect, which leads to spectral branch terms. It causes two essential effects. The first is the splitting of multiple levels, referred to as zero-field splitting or fine structure splitting. The energy separation between the multiple components increases strongly with growing nuclear charge. Second, SOC mixes electronic states of different multiplicities, thus allowing radiant transitions (phosphorescence) and non-radiant transitions (intersystem crossing) between them. Phosphorescence and intersystem crossing rates determine, for instance, the lifetime of the first electronically excited triplet state of an organic molecule. The availability of molecules in this state plays a key role in photochemical reactions, photosynthesis, and the photo-biological activity of drugs, luminescence, etc.

SOC is important for studying the spectrum branch terms of molecules and their electric states.[3−5] The study on the hydrides (MgH, AlH^+, SiH, PH^+, SH, ClH^+) under SOC is five-fold in purpose. First, the MgH has assumed increasing importance in astrophysics over the past four decades, it has been extensively studied both[6−10] experimentally, using electronic spectroscopy, and theoretically, using *ab initio* techniques. Much of the interest in MgH is linked with its astrophysical importance because it has been observed, for example, in the atmospheres of cool stars,[11] and in the photosphere of the sun.[12,13] Secondly, aluminium containing compounds have received increased attention in recent years because of their use in solid propellants and explosives. A number of experimental and theoretical studies on the spectroscopy, kinetics and energetic of several aluminium containing species have been reported, spectroscopic constants have been studied for states $X^2\Pi$ of AlH^+[14] and AlH^-,[15] the spin splitting for AlH^+ had been studied theoretically,[16] and the hyperfine parameters for aluminium hydride[17] and the heats of formation for aluminium containing compounds[18] have been studied. Thirdly, SiH is a free radical of fundamental importance. In recent years, there have been numerous experimental and theoretical studies of SiH because of its importance in astrophysics.[19] Because of significant cosmic abundances of Si and H, there is a strong possibility that the SiH radical may be found in the interstellar medium and stellar atmospheres.[20] SiH has al-

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ready been identified in the spectra of sunspots.[21−23] Fourthly, atmospheric oxidation of sulfur species released through anthropogenic and biogenic sources has received special attention in recent years due to its potential connection with environmental processes such as acid rain, climate modification, the greenhouse effect, and ozone layer depletion, hydrogen sulfide plays a central role, and an important intermediate in the oxidative process of this compound is the radical HS, its dehydrogenation condensation and observed rotational spectrum[24] for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ splitting of the $X^2\Pi$ of HS have been given. Fifthly, phosphine is a toxic gas and an important chemical reagent, and it is an amphoteric chemical which hydrolyzes only with concentrated acids or bases. Although there are many studies concerning the (MgH, AlH^+, SiH, PH^+, SH, ClH^+) species mentioned above, the spectroscopic constants and potential energy functions for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ split state of the $^2\Pi$ state have seldom been given up to now. Here we present a study of the spectroscopic constants and potential energy functions of individual spin-orbit-split components of the $^2\Pi$ states for the molecules based on spin-orbit Multi-Configuration Quasi-Degenerate Perturbation Theory (SO-MCQDPT), i.e., the MCQDOPT method with SOC. This method has been proven to be feasible for computing the splitting of molecular electronic states using the Gamess-US program. A widely used non-relativistic approach appends the approximate Breit-Pauli SOC operator is treated as a perturbation. This approximation is found to be reasonable for systems where the spin-orbit interaction is weak or moderate.[1]

In this paper, the energy level splitting for the hydride molecules (cations) of the third period under SOC is studied theoretically using the Gamess-US suite with the SO-MCQDPT method. This paper is organized as follows: in Section 2 the SO Hamiltonian is briefly introduced and the equations for the Murrell–Sorbie (M–S) potential energy function and the spectroscopic data listed directly without derivation. In Section 3, the SO-MCQDPT method is applied to oxygen atom and hydride molecules (cations) (MgH, AlH^+, SiH, PH^+, SH, ClH^+), and the results are compared with the experimental values. The conclusions are in Section 4.

2. Computational details

2.1. H^{SO} operator and SO-MCQDPT method

Since the common theoretical models for molecular calculations are single-component codes with the solution of the non-relativistic Schrödinger equation, it is reasonable to include SO and other relativistic corrections in these models. The Foldy–Wouthuysen transformation[25] for the Dirac–Coulomb equations is to eliminate the two small component spinors corresponding to positrons, producing a two-component equation, and may further eliminate the spin dependence of the Hamiltonian making it spin free (H^{SF}), thereby eliminating a third component and producing a single-component equation. This transformation, truncated at order $1/c^2$, leads to the following H^{SO} operator. The total Hamiltonian operator H could be expressed as

$$H = H^{\mathrm{SF}} + H^{\mathrm{SO}}. \tag{1}$$

The well-known non-relativistic Schrödinger operator contains kinetic energy and coulomb terms. The spin-independent mass-velocity H^{MV}[26] and Darwin H^{D}[26] relativistic corrections (whose two-electron term is often neglected) are often termed 'scalar' relativistic effects and can be used to define the spin-free Hamiltonian, also known as the Cowan-Griffin[27] operator,

$$H^{\mathrm{SF}} = H^{\mathrm{NR}} + H^{\mathrm{MV}} + H^{\mathrm{D}}, \tag{2}$$

The final term of the H operator at order $1/c^2$ is the SOC term, known as the Breit–Pauli SO operator,

$$H^{\mathrm{SO}} = \frac{1}{2m^2c^2}\left[\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}^3}\widehat{\boldsymbol{L}}_{i\alpha}.\widehat{\boldsymbol{S}}_i - \sum_i\sum_j \frac{e^2}{r_{ij}^3}\widehat{\boldsymbol{L}}_{ij}.(\widehat{\boldsymbol{S}}_i + 2\widehat{\boldsymbol{S}}_j)\right]. \tag{3}$$

This contains both one- and two-electron terms. In these formulae, $\widehat{\boldsymbol{L}}$ and $\widehat{\boldsymbol{S}}$ are space and spin angular momentum operators, $\widehat{\boldsymbol{L}}_{j\alpha} \equiv (\boldsymbol{r}_i - \boldsymbol{R}_\alpha) \times \boldsymbol{P}_i$, $\widehat{\boldsymbol{L}}_{ij} \equiv (\boldsymbol{r}_i - \boldsymbol{r}_\alpha) \times \boldsymbol{P}_i$, Roman and Greek subscripts denote electrons and nuclei respectively. The above models are incorporated into the transition directive of Gamess-US.

Equation (3) gives the full Breit–Pauli SOC operator, corresponding to the HSO_2 directive in Gamess-US package. If the active–active two-electron contributions to H^{SO} of equation (3) are omitted, the corresponding model is called HSO_2P, i.e. only partial two-electron and full one-electron contributions are included in the directive HSO_2P. Our calculation is to retain all active–active two-electron contributions in H^{SO} for the full Breit-Pail operator, therefore, the results are theoretically expected to be better than those of calculations using HSO_2P, and the latter is employed by Fedorov and Gordon.

In this work the SO-MCQDPT method is employed using the GAMESS-US procedure. SO-MCQDPT is based on single and double excitations from the complete active space (CAS) and the SOC. The Hamiltonian is constructed in the basis of a few CAS configuration interaction (CI)[28−33] states, with the perturbations built now into the effective SOC Hamiltonian. The MCQDPT method based on M$\not$ller–Plesset[34] partitioning as proposed by M$\not$ller and Plesset, is a multi-state, as well as multi-reference (MR) perturbation theory. It has several advantages over other MR methods. Firstly, it is more efficient than other MR based methods such as MR-CI and MR-CC, because it does not require diagonalization iterations or solving linear equations. Secondly, it can yield results within chemical accuracy. Thirdly, it can describe open shell or excited states as well as closed shell ground states in a single framework.

The 6-311+g (3p) and 6-311+g (3df) basis sets are used for H and elements of the third period, respectively.

2.2. Potential energy function

Molecular potential energy function is a molecular structure for full space and plays a key role in molecular collision. All the potential energy functions for the splitting of low-lying states are least-square fitted as the Murrell–Sorbie (M–S) function[35,36]

$$V(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \quad (4)$$

where $\rho = R - R_e$, R is the inter-atomic distance, and R_e is the equilibrium distance. From the M–S function it is easy to derive f_2, f_3 and f_4, and then calculate the spectroscopic parameters B_e, ω_e, α_e, $\omega_e\chi_e$ using Eqs.(5)–(11). The corresponding formulae are

$$f_2 = D_e(a_1^2 - 2a_2), \quad (5)$$

$$f_3 = D_e(a_1a_2 - a_3 - a_1^3/3), \quad (6)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \quad (7)$$

$$B_e = h/8\pi^2c\mu R_e^2, \quad (8)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \quad (9)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \quad (10)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \quad (11)$$

3. Results and discussions

3.1. Oxygen atom

Firstly, oxygen is taken as an example to prove the validity of the SO-MCQDPT method. The comparison between the calculated values and the experimental result[37] is listed in the Table 1.

Table 1. Energy levels for oxygen atom (^3P).

Configuration	State	J	Experiment/cm^{-1}		Calculation/cm^{-1}	
			Level	Interval	Level	Interval
$2s^22p^4$	^3P	2	0.000	–158.265	0.00(2)	–155.208
					1.257	
					1.265	
					1.684	
		1	158.265	–68.712	155.208	–72.100
					155.217	
					155.339	
		0	226.977		231.130	

From the Table 1, it can be seen that the energy levels split owing to the relativistic effect–SOC, the ground state ^3P term of the configuration $2s^22p^4$ for O splits into three different J levels, $^3P_2$, $^3P_1$ and $^3P_0$. Comparing the calculated values with experimental values in the Table 1, we can see that the calculated results are in better agreement with experimental values by using Gamess-US to process

the low-lying states, for example, the errors for $^3P_1$ are 2.08%, 2.07%, 1.99% and for $^3P_0$ is 1.99%, respectively. This method will be extended to hydride molecules (cations) in view of this calculated result.

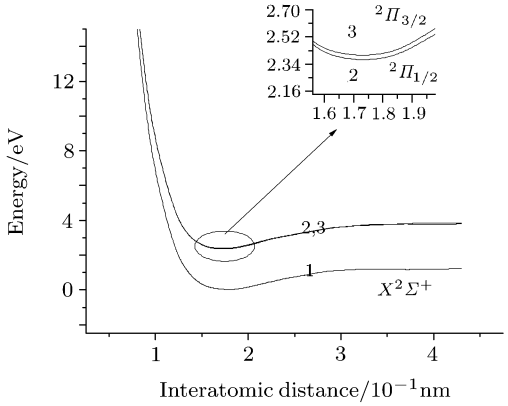
3.2. Hydride molecules (cations)

For linear molecules under SOC, the coupling of electronic states[38] can be expressed as

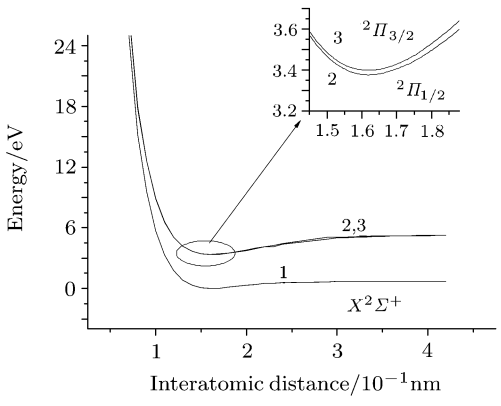
$$\Omega = |\Lambda + \Sigma|, \tag{12}$$

where Λ and Σ are orbit and spin angular momentum, respectively. Under SOC, the state $^2\Pi$ splits into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ for $\Lambda = 1$, $\Sigma = \pm 1/2$, and $^2\Delta$ splits into $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ because of $\Lambda = 2$, $\Sigma = \pm\frac{1}{2}$.

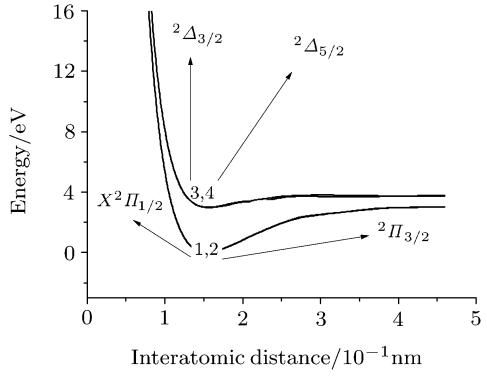
The calculated results are in agreement with the above prediction, Fig.1 shows the details of the potential energy curves for the split states of low-lying or low excited states for hydride molecules (cations) of



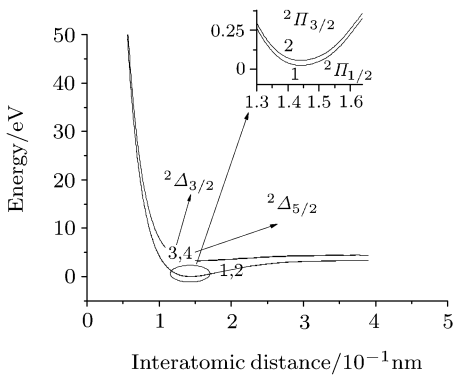
(a) The potential energy curve of MgH



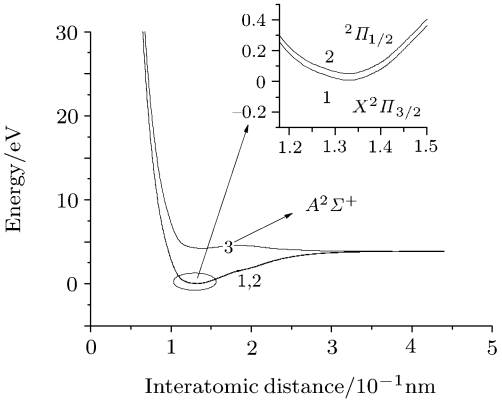
(b) The potential energy curve of AlH^+



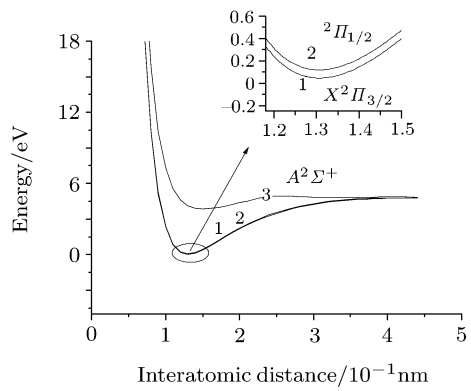
(c) The potential energy curve of SiH



(d) The potential energy curve of PH^+



(e) The potential energy curve of SH



(f) The potential energy curve of ClH^+

Fig.1. The potential energy curves of hydride of the third period.

the III period. The parameters R_e and D_e of the potential energy functions for the corresponding states also are worked out by the least-squares fitting. Moreover, the force constants and the spectroscopic constants for these three states can be derived out using Eqs.(5)–(11). All those data are listed in Table 2.

Table 2. Parameters of the analytical potential function and spectroscopic data.

(a) MgH

State	D_e/cm^{-1}	R_e/nm	T_e/eV	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$X^2\Sigma^+$ MCQDPT	1.1420	0.172	0.000	1494.55	44.627	5.9065	0.2329	
$X^2\Sigma^{+[14]}$	1.3400	0.173	0.000	1495.20	31.889	5.8257	0.1859	
$X^2\Sigma^{+[10]}$				1484.4	30.989	5.7177	0.1453	
$^2\Pi_{1/2}$ MCQDPT	1.4945	0.170	2.231	1534.6	41.585	6.0676	0.2243	953.444
$^2\Pi_{3/2}$ MCQDPT	1.5245	0.170	2.350	1513.8	41.130	6.0310	0.2249	
$^2\Pi^{[14]}$		0.168	2.389	1598.17	31.085	6.1913	0.1931	
$^2\Pi^{[10]}$	1.6040	0.170	2.377	1561.8	33.170	6.0373	0.1768	
$^2\Pi^{[39,40]}$	1.6980	0.168	2.384	1599.5	32.536	6.1913	0.1931	

(b) AlH^+

State	D_e/cm^{-1}	R_e/nm	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$X^2\Sigma^+$ MCQDPT	1.0139	0.1600	0.00	1600.47	81.7335	6.7779	0.3945	
$X^2\Sigma^{+[14]}$		0.1602	0.00	(1620)*		6.7630	0.3980	
$^2\Pi_{1/2}$ MCQDPT	1.9640	0.1600	27076.14	1702.50	46.9956	6.7779	0.2668	204.325
$^2\Pi_{3/2}$ MCQDPT	1.9292	0.1600	27280.46	1743.46	45.0761	6.7779	0.2489	
$A^2\Pi^{[14]}$		0.1591	(27593)*	(1770)*		6.7630	0.2480	
			(27686)*					

(c) SiH

State	D_e/cm^{-1}	R_e/nm	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$X^2\Pi_{1/2}$ MCQDPT	3.0683	0.1500	0.0	2116.22	44.06	7.7019	0.2447	118.516
$^2\Pi_{3/2}$ MCQDPT	3.1181	0.1500	118.5	2165.33	42.36	7.7019	0.2278	
$X^2\Pi_r^{[14]}$	$D_0^0 \leq 3.0602$	0.15201	0.0	2041.80	35.51	7.4996	0.2190	
$X^2\Pi_r^{[35]}$	3.1850	0.1520						
$X^2\Pi_r^{[41]}$	3.126111	0.1520		2057.8	37.8	7.505	0.218	
$X^2\Pi_r^{[42]}$	3.14–3.19	0.151966(7)		2042.5229(8)	36.0552(5)	7.503898	0.21814(2)	
$X^2\Pi_r^{[43]}$	3.040250	0.1544		2015	39.0	7.269	0.208	
$X^2\Pi_r^{[44]}$		0.1520		2022				
		0.1523		2062				
$X^2\Pi_r^{[45]}$		0.152142		2062	38.5		0.21755	
$X^2\Pi_r^{[46]}$	2.858989			2181.24				
$X^2\Pi_r^{[47]}$	3.148226	0.151521		1949				
$X^2\Pi_r^{[48]}$		0.1541		1996.4	28.94			
$X^2\Pi_r^{[49,50]}$		0.15201						
$X^2\Pi_r^{[51]}$	3.174245	0.152142						
$X^2\Pi_r^{[52]}$	3.061932	0.15259						
$X^2\Pi_r^{[53]}$	3.161236	0.15236		2036.2	35.8		0.2148	
$X^2\Pi_r^{[54]}$		0.1533		2050				
$X^2\Pi_r^{[55]}$	3.192024	0.1521						
$X^2\Pi_r^{[56]}$		0.1503						
$X^2\Pi_r^{[57]}$	3.197228	0.15221		2043.15	35.09		0.213	
$^2\Delta_{3/2}$ MCQDPT	0.8010	0.1600	24045.6	1406.12	74.28	6.7693	0.4489	153.261
$^2\Delta_{5/2}$ MCQDPT	0.7399	0.1600	24045.7	1393.48	76.94	6.7693	0.4621	
$A^2\Delta^{[14]}$		0.152347	24300.4	1858.90	99.175	7.4664	0.3445	

Table 2. (Continued).

(c) SiH

State	D_e/cm^{-1}	R_e/nm	T_e/eV	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$A^2\Delta$[58]		0.1554		1955				
$A^2\Delta$[43]	0.86988	0.1546		1797	91.0		0.420	
$A^2\Delta$[41]		0.1517		1884.4	68.4		0.242	
$A^2\Delta$[49]		0.15201						
$A^2\Delta$[57]	0.97352	0.15237		1853.15	78.39		0.375	
$A^2\Delta$[59]	0.8924–0.9406	0.15197816(21)				7.502718(21)	0.215119(15)	

(d) PH^+

State	D_e/cm^{-1}	R_e/nm	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$^2\Pi_{1/2}$ MCQDPT	3.357	0.1400	0.00	2536.10	52.3500	8.8117	0.2667	258.25
$^2\Pi_{3/2}$ MCQDPT	3.361	0.1400	258.25	2534.65	52.3299	8.8117	0.2669	
$X^2\Pi$[14]	≤ 3.36	0.1435	0.00	2299.60		8.3851		
$^2\Delta_{3/2}$ MCQDPT	1.25	0.1550	25941.66	1607.68	60.3172	7.1888	0.3741	51.32
$^2\Delta_{5/2}$ MCQDPT	1.162	0.1550	26253.78	1539.76	65.4715	7.1888	0.4196	
$^2\Delta$[14]		0.1573	26221*	1398.76		6.9833		

(e) SH

State	D_e/cm^{-1}	R_e/nm	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$X^2\Pi_{3/2}$ MCQDPT	3.982	0.1300	0.000	3025.3	61.4	10.2095	0.299	354.00
$^2\Pi_{1/2}$ MCQDPT	3.966	0.1300	344.996	3047.6	62.5	10.2095	0.299	
$X^2\Pi_i$[14]	3.556*	0.1341	0.000	2711.6*	59.9*	9.4611*	0.270*	
$X^2\Pi_i$[35]	3.716	0.1341						
$X^2\Pi_i$[60]		0.1343		2702	57	9.56	0.280	
$X^2\Pi_i$[61]	3.529	0.1342		2739	55.1	9.59	0.29	
$X^2\Pi_i$[62]		0.1346		2755	58.5			
$X^2\Pi_i$[63]	3.700	0.1340		2702	60	9.611	0.300	
$X^2\Pi_i$[64]		0.1341		2711.6	59.9	9.600	0.270	
$X^2\Pi_i$[65]		0.1340		2695.8	48.5	9.6036	0.2786	
$X^2\Pi_i$[66]		0.1341		2696.2	48.74	9.6002	0.2799	
$X^2\Pi_i$[67]	3.736	0.1345		2704.2	51.88	9.5482	0.2031	

(f) ClH^+

State	D_e/cm^{-1}	R_e/nm	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	ν_{ee}/cm^{-1}
$^2\Pi_{1/2}$ MCQDPT	4.768	0.1300	0.000	2653.31	53.633	10.1827	0.3593	589.247
$^2\Pi_{3/2}$ MCQDPT	4.727	0.1300	589.247	2666.58	53.577	10.1827	0.3553	
$X^2\Pi$[14]	≤ 4.656	0.1315	0.000	2673.69	52.537	9.9566	0.3272	

* Uncertain data.

The geometric structures for the split state of hydride molecules (cations) of the third period are worked out for the first time up to now. The equilibrium distance is the same as the split states of the same state, for example, the equilibrium distance of $A^2\Pi_r$ (MgH) for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ split states is the same R_e=1.700Å in our research, besides, the calculated result also gives the size of the energy for the split states. All the energies of the split states in the same nuclear distance are listed in Table 3.

Table 3. The energies of the split states.

Molecules (cations)	state	split state	Energy/a.u.	Interval of split energy/cm^{-1}	Exp.[14]/cm^{-1}
MgH MCQDPT	$A^2\Pi_r$	$^2\Pi_{1/2}$	–200.1165	28.8	25.3
		$^2\Pi_{3/2}$	–200.1122		
AlH^+ MCQDPT	$A^2\Pi_r$	$^2\Pi_{1/2}$	–242.1275	173	108
		$^2\Pi_{3/2}$	–242.1265		
SiH MCQDPT	$X^2\Pi_r$	$^2\Pi_{1/2}$	–38.4080	230	143
		$^2\Pi_{3/2}$	–38.4078		
PH^+ MCQDPT	$X^2\Pi_r$	$^2\Pi_{1/2}$	–341.0533	260	296
		$^2\Pi_{3/2}$	–341.0521		
SH MCQDPT	$X^2\Pi_i$	$^2\Pi_{3/2}$	–398.2045	–342	–377
		$^2\Pi_{1/2}$	–398.2029		
ClH^+ MCQDPT	$X^2\Pi_i$	$^2\Pi_{3/2}$	–459.7882	–590	–648
		$^2\Pi_{1/2}$	–459.7855		
OH[3] MCQDPT	$X^2\Pi_i$	$^2\Pi_{3/2}$	–75.5487	–141	–139
		$^2\Pi_{1/2}$	–75.541		

In the Table 3, the split states of hydride molecules (cations) are listed in the energy order, it can be found that the splitting of same state $^2\Pi$ has two schemes based on the subscript of state $^2\Pi$. For example, the $^2\Pi_{1/2}$ is lower state and the $^2\Pi_{3/2}$ is higher state if the subscript of the $^2\Pi$ is 'r', the result is opposite if the subscript is 'i', which is relative to molecular electric configuration.

For the split states of $^2\Pi$, the spectroscopic data and the parameters of the analytical potential functions are quite accurate based on the experimental result, nevertheless the theoretical calculation errors on the splitting states of state $A^2\Delta$ (SiH, PH^+) are a little bit larger, the reason might be due to the selection of the CAS and the limitation of the basis set. With the use of large active space and big basis set, the calculated result is likely to be improved further, but this process is quite time-consuming.

The energy interval of SOC between $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ is also given in our calculation, the result in the same nuclear distance is listed in the fifth row of the Table 3. From the fifth row, it can be seen that the energy interval of SOC between $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ increases with element nuclear charge Z. For example, from MgH to AlH^+ to SiH to PH^+ to SH to ClH^+ the interval value varies from 28.8 to 173 to 230 to 260 to (–342) to (–590)(cm^{-1}), the variety is in agreement with the experimental value listed in the last row.

4. Conclusion

The theoretical researches of molecular structure for hydride molecules (cations) of the third period under SOC have been worked using the method of SO-MCQDPT in Gamess-US package.

The calculations for the three sublevels $^3P_2$, $^3P_1$, $^3P_0$ of the ground term ^3P of oxygen atom are in well agreement with the experimental values. These results directly justify the feasibility of the SO-MCQDPT method. For the first time, the theoretical studies on the splitting for hydride molecules (cations) of the third period under SOC and potential energy curves for the split states have been fitted at the least-squaring with M–S analytical function, besides, the spectroscopic parameters for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ split states have been derived in our research. The calculated vertical transition energy from $^2\Pi_{1/2}$ to $^2\Pi_{3/2}$ at the same nuclear distance is driven in this paper. The result tests that the energy interval of SOC for the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states increases with element nuclear charge Z in the same period in our research.

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