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The splitting of low-lying states for hydroxyl molecule under spin–orbit coupling*

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The splitting of potential energy curves for the states $X^2\Pi_{3/2}$, $^2\Pi_{1/2}$ and $A^2\Sigma^+$ of hydroxyl OH under spin–orbit coupling (SOC) has been calculated by using the SO multi-configuration quasi-degenerate perturbation theory (SO-MCQDPT). Their Murrell–Sorbie (M–S) potential functions have been derived, then, the spectroscopic constants for $X^2\Pi_{3/2}$,$^2\Pi_{1/2}$ and $A^2\Sigma^+$ have been derived from the M–S function. The calculated dissociation energies for the three states are $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=34966.632cm^{-1}, $D_0[\mathrm{OH}(^2\Pi_{1/2})]$=34922.802cm^{-1}, and $D_0[\mathrm{OH}(A^2\Sigma^+)]$=17469.794cm^{-1}, respectively. The vertical excitation energy $\nu[^2\Pi_{1/2}(\nu=0)\rightarrow X^2\Pi_{3/2}(\nu=0)]$ = 139.6cm^{-1}. All the spectroscopic data for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are given for the first time except the dissociation energy of $X^2\Pi_{3/2}$.

Keywords: SOC, SO–MCQDPT method, spectroscopic constants, OH radical
PACC: 3150, 7170E

1. Introduction

Spin–orbit coupling (SOC)[1] is a kind of magnetic effect, and in fact, a relativistic effect, which lead 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 greatly 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, and so on.

OH radical molecule is a basic functional group for organic molecules and of interest for chemical reaction process. Both the generation and annihilation of the great mass of pollutants in the atmosphere have a certain relation with OH. Besides, it is one of the most important oxidizer in the troposphere and has important effects[1,2] on formation of acid rain and ullage of ozone and so on. The research of hydroxyl is of great importance in the domains of environment science, spectroscopy, Cosmo chemistry etc.

The radical molecule OH is being studied by many researchers in the recent 50 years. The electronic structures and their corresponding properties of the electronic states $X^2\Pi$ and $A^2\Sigma^+$ have been intensively studied in both experimental and theoretical[3–5] studies on bond-space, oscillation frequency, dissociation energy, etc. However, up to now, the potential energy curves and spectroscopic constants on the electronic states $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are seldom studied, except for the dissociation energy of $\mathrm{OH}(X^2\Pi_{3/2})$. In experiment, there are lots of experiment results on the dissociation energy of $\mathrm{OH}(X^2\Pi_{3/2})$, for examples, $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$ is derived by Barrow[3] in 1956 and by Ruscic *et al* [4] indirectly based on pulsed-field-ionization

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photoelectron spectroscopy measurements and mass-selected photo-ionization measurements in 2002. The Barrow result $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=35427cm^{-1} is accepted widely and the Ruscic photo-ionization experimental value $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=35593±24cm^{-1} are in good agreement with their own calculation. In theory, Ruscic and co-workers carried out a CCSD(T)/aug-cc-pVnZ *ab initio* calculation on OH using MOLPRO, Gaussian 98, and ACES-II and got a $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=35532cm^{-1} in corroboration of their experiment value; Joens[5] analysed the available experimental data for thermodynamic cycles involving H_2O and H_2O_2 and obtained the value $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=35584±10cm^{-1}, which reduces the uncertainty in the values reported by Ruscic and co-workers by a factor of 3; and Zhou *et al* [6] gave a $D_0[\mathrm{OH}(X^2\Pi_{3/2})]$=35565±30cm^{-1} in 2003. Nevertheless, the other spectroscopic constants and the potential energy curves for the two split states $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ of OH have never been covered by experimental and theoretical studies, the only exception being the vertical excitation energy from $^2\Pi_{1/2}(\nu=0)$ to $X^2\Pi_{3/2}(\nu=0)$ listed in Herzberg's Handbook of 1979. In view of the above, the all spectroscopic constants and the potential energy structures corresponding to the splitting of low-lying states for the OH radical molecule will be calculated in the present research based on SO multi-configuration quasi-degenerate perturbation theory (SO-MCQDPT), i.e., the method MCQDOPT with spin–orbit Coupling (SOC). This method has been proven to be feasible to work out the splitting of molecular electronic states using the Gamess-US.[7]

In this paper, the energy level splitting for OH molecule under SOC will be theoretically studied using the Gamess-US suite with SO-MCQDPT. Besides its importance mentioned above, the small number of electrons and the wealth of existing experimental data for the OH molecule are also beneficial to the quick calculation and the comparison with the calculation results. The paper is organized as follows: in Section 2 the SO Hamiltonian is briefly introduced and the equations for the M–S potential energy function and the spectroscopic data listed directly without derivation. In Section 3, the SO-MCQDPT method is applied to the oxygen atom and OH radical molecule, and the results are compared with the experiment values. Conclusions are given in Section 4.

2. Computational details

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

Since the common theoretical models for molecular calculation 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[8] 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

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

First, the well-known non-relativistic Schrödinger operator is

$$H^{\mathrm{NR}} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i\sum_\alpha Z_\alpha e^2/r_{i\alpha} + \sum_i\sum_i e^2/r_{ij} + \sum_\alpha\sum_\beta Z_\alpha Z_\beta e^2/r_{\alpha\beta}. \tag{2}$$

The spin-independent mass-velocity and Darwin relativistic corrections (whose two-electron term is often neglected) are given as follows:

$$H^{\mathrm{MV}} = -\frac{\hbar^4}{8c^2m^3}\sum_i \nabla_i^4, \tag{3}$$

$$H^{\mathrm{D}} = -\frac{\pi\hbar^2}{2m^2c^2}\left[\sum_i\sum_\alpha Z_\alpha e^2\delta(r_{i\alpha})\right]. \tag{4}$$

These are often termed 'scalar' relativistic effects and which could be used to define the spin-free Hamiltonian, also known as the Cowan–Griffin operator,

$$H^{\mathrm{SF}} = H^{\mathrm{NR}} + H^{\mathrm{MV}} + H^{\mathrm{D}}. \tag{5}$$

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

$$H^{\mathrm{SO}} = \frac{1}{2m^2c^2}\left[\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}^3}\widehat{I}_{i\alpha}.\widehat{S}_i - \sum_i\sum_j \frac{e^2}{r_{ij}^3}\widehat{I}_{ij}.(\widehat{S}_i + 2\widehat{S}_j)\right], \tag{6}$$

which contains both one- and two-electron terms. In these formulae, $\widehat{I}$ and $\widehat{S}$ are space and spin angular momentum operators, $\widehat{I}_{j\alpha} \equiv (r_i - R_\alpha) \times P_i$,

$\widehat{I}_{ij} \equiv (r_i - r_\alpha) \times P_i$, Roman and Greek subscripts denote electrons and nuclei respectively. The above models are incorporated into the transition directive of Gamess-US.

Equation (6) is the full Breit–Pauli operator, corresponding to the HSO2 directive in Gamess-US package. If the active-active two electron contributions to H^{SO} of equation (6) is omitted, the corresponding model is called HSO2P, i.e. only partial two electron and full one-contribution are included in the directive HSO2P. Our calculation is to retain all active-active two electron contribution in H^{SO} in full Breit–Pauli operator, therefore, the results are theoretically expected to be better than those of calculations using HSO2P; the latter is employed by Fedorov and Gordon.[9]

In the present work the SO-MCQDPT method is employed in GAMESS-US procedure. SO-MCQDPT is based on single and double excitations from the CAS and the SOC. Hamiltonian is constructed in the basis of a few CASCI states, with the perturbations built now into the effective SOC Hamiltonian. The MC-QDPT method based on Møller–Plesset partitioning is proposed by Møller and Plesset:[10] it 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 the other MR based methods such as MR-CI and MR coupled cluster (MR-CC), because it does not require iterations for diagonal or for 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 configuration interaction and spin–orbit coupling for the two low-lying states $X^2\Pi$ and $A^2\Sigma^+$ are studied in present research. The ground electronic configuration of hydroxyl state $X^2\Pi$ is $(1s)^2(2s\sigma)^2(2p\sigma o + 1s_H)^2\ (2P\pi\ o)^2\ (2P\pi\ o)^1$, if one electron is transferred from the orbit $(2p\sigma o{+}1s_H)$ to the orbit $(2P\pi o)$, the first excited state $(A^2\Sigma^+)$ will be formed, and its configuration will be $(1s)^2(2s\sigma)^2(2p\sigma o{+}1s_H)^1(2P\pi o)^4$. In the present research, we have calculated the structure of the above two states under SOC, the spectroscopic parameters and potential energy functions, respectively. The 6-311+g (3p) and 6-311+g (3df) basis sets are used for H and O atoms, 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 function[11,12]

$$V(\rho) = -D_{\mathrm{e}}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \quad (7)$$

where $\rho = R - R_{\mathrm{e}}$, R is the inter-atomic distance, R_{e} is its equilibrium distance. From the M–S function it is easy to derive f_2, f_3 and f_4, and then calculate spectroscopic data $\omega_{\mathrm{e}}, \omega_{\mathrm{e}}\chi_{\mathrm{e}}, B_{\mathrm{e}}, \alpha_{\mathrm{e}}$ using equations (7)–(13). The corresponding formulae are

$$f_2 = D_{\mathrm{e}}(a_1^2 - 2a_2), \quad (8)$$

$$f_3 = D_{\mathrm{e}}(a_1a_2 - a_3 - a_1^3/3), \quad (9)$$

$$f_4 = D_{\mathrm{e}}(3a_1^4 - 12a_1^2a_2 + 24a_1a3), \quad (10)$$

$$B_{\mathrm{e}} = h/8\pi^2 c\mu R_{\mathrm{e}}^2, \quad (11)$$

$$\omega_{\mathrm{e}} = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \quad (12)$$

$$\alpha_{\mathrm{e}} = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \quad (13)$$

$$\omega_{\mathrm{e}}\chi_{\mathrm{e}} = \frac{B_{\mathrm{e}}}{8}\left[-\frac{f_4R_{\mathrm{e}}^2}{f_2} + 15\left(1 + \frac{\omega_{\mathrm{e}}\chi_{\mathrm{e}}}{6B_{\mathrm{e}}^2}\right)^2\right]. \quad (14)$$

3. Results and discussions

3.1. Oxygen atom

Firstly, oxygen is taken as an example to prove the validity of the SO-MCQDPT method. Comparison between the calculation values and the experiment results is listed in Table 1.

From 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 $^3P_0$. The $^3P_2$ splits into five different levels and $^3P_1$ splits into three different levels because of the basis sets. Comparing the calculated values with experiment values in the Table 1, we can see that the calculated results are in better agreement with experiment values by using Gamess-US to process the low-lying states. This method will be extended to hydroxyl radical in view of this calculation result.

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

Configuration	State	J	Experiment/cm^{-1}		Calculation/cm^{-1}	
			Level	Interval	Level	Interval
$2s^22p^4$	^{3}P	2	0.0	–158.5	0.00(2)	
					1.2574	155.2077
					1.2651	
					1.6836	
		1	158.5	–68.5	155.2077	
					155.2167	72.1
					155.3387	
		0	226.5		231.13	

3.2. Hydroxyl radical molecule

For linear molecules under SOC, the coupling of electronic states[13] can be expressed as

$$\Omega = |\Lambda + \Sigma|, \tag{15}$$

where Λ and Σ are orbit and spin angular momentum, respectively. Under SOC, the $X^2\Pi$ state is split into $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ for $\Lambda = 1, \Sigma = \pm 1/2$ and there is no split for $A^2\Sigma^+$ because of Λ=0, Σ=1/2.

The calculation results are in agreement with the above prediction, Fig.1 shows the details of the potential energies for the states $X^2\Pi_{3/2}$, $^2\Pi_{1/2}$ and $A^2\Sigma^+$. The parameters a_1, a_2, a_3, 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.(7)–(13). All those data are listed in Table 2 and Table 3, respectively.

Table 2. Parameters of the analytical potential function.

Electronic state	R_e/Å	a_1/Å^{-1}	a_2/Å^{-2}	a_3/Å^{-3}	D_e/cm^{-1}
$X^2\Pi_{3/2}$ MCQDPT	0.9640	4.7596	5.8567	4.5197	36839.013
$^2\Pi_{1/2}$ MCQDPT	0.9640	4.7675	5.8808	4.5259	36796.427
$X^2\Pi$[11]	0.9696	4.5070	4.8840	3.7950	37270.597
$A^2\Sigma^+$ MCQDPT	1.0	3.3099	–2.9951	–0.0073	19136.246

Table 3. Spectroscopic data.

State	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	R_e/nm	D_0/cm^{-1}	ν_{00}/cm^{-1}
$X^2\Pi_{3/2}$ MCQDPT	3785.890	82.255	19.133	0.7066	0.0964	34966.632	
$X^2\Pi_{3/2}$ Exp.						35450±100[3]	
						35593±24[4]	
						35584±10[5]	
						35565±30[6]	
						35420±15[14]	
$^2\Pi_{1/2}$ MCQDPT	3788.404	82.308	19.133	0.7054	0.0964	34922.802	139.60
$^2\Pi_{1/2}$ Exp.							126.23[15]
$X^2\Pi$ Exp.[15]	3737.760	84.881	18.910	0.7242	0.096966		
$A^2\Sigma^+$ MCQDPT	3395.849	125.89	17.781	0.8910	0.10000	17469.794	
Exp.[15]	3178.80	92.91	17.358	0.7860	0.10121	18956±14[4]	
						19011±10[5]	
						18943±30[16]	

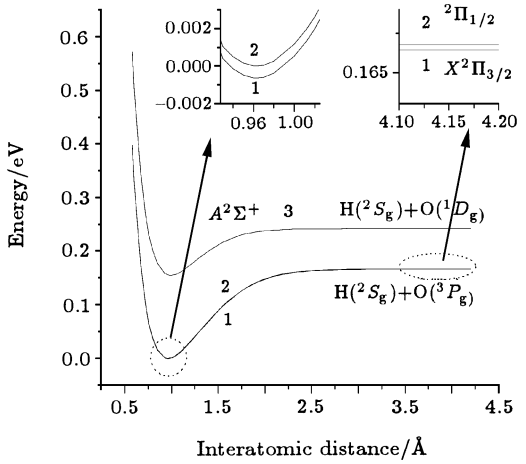


Fig.1. The PECs of the ground state $X^2\Pi(1, 2)$ and the first excited state $A^2\Sigma^+(3)$ of OH and the partly magnified PECs of the states $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ of OH.

The geometric structures for $X^2\Pi_{3/2}$,$^2\Pi_{1/2}$ are worked out for the first time up to now. The equilibrium distance of OH molecule for the two states $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ is the same R_e=0.964Å in our research, besides, the calculation result also shows that the $X^2\Pi_{3/2}$ is the ground state and the $^2\Pi_{1/2}$ is the first excited state under the spin–orbit coupling, this is because $E(X^2\Pi_{3/2})$=–75.5486921733 a.u. is lower than $E(^2\Pi_{1/2})$=–75.5480560145 a.u. at the equilibrium distance. From the calculated results in Table 3, the dissociation energies for the two states are also given in the present research, which are $D_0(X^2\Pi_{3/2})$ = 34966.632cm^{-1} and $D_0(^2\Pi_{1/2})$ = 34922.802cm^{-1}, respectively. The deviation from the up to date reported result for the dissociation energy of $X^2\Pi_{3/2}$ is 568.4–628.4cm^{-1}(1.6%–1.76%). As can be seen in Table 3, the error for $A^2\Sigma^+$ is a little bit larger, the reason might be due to the selection of the CAS and the limitation of the basis set. With the using of large complete active space and basis set, the calculation result is likely to be improved further, but this process is quite time-consuming.

3.3. The Energy Interval of SOC between $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ for OH

The splitting energy intervals between $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ have been presented in Fig.2. This energy interval could be regarded as vertical transition energy from $X^2\Pi_{3/2}$ to $^2\Pi_{1/2}$, as with the increasing of OH inter-atomic distance, the curve experienced a little increasing from 0.5Å to 1.55Å, and then a gradual decreasing to about 67.5cm^{-1} at 4.2Å. The energy interval could also be approximately regarded as the SOC energy of $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, the results show that the energy difference at all distances of OH molecule is lower than 141cm^{-1}. This result indicates that perturbation approximation of SOC is reasonable for the light molecules.

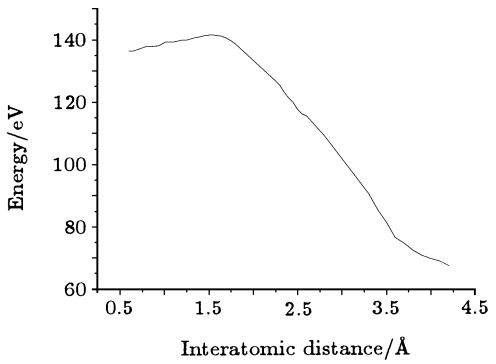


Fig.2. The curve of the vertical transition energy of OH $X^2\Pi_{3/2\rightarrow1/2}$ vis the inter-atomic distance.

4. Conclusion

The theoretical research of molecular structure for hydroxyl radical under SOC have been worked out 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 good agreement with the experiment values. These results directly justify the feasibility of the SO-MCQDPT method. For the first time, the theoretical studies on the splitting of $X^2\Pi$ of hydroxyl radical molecule under SOC and potential energy curves for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ have been fitted by the least-squaring with M–S analytical function, and the spectroscopic parameters for the two states have been derived in our research. The calculated vertical transition energy from $^2\Pi_{1/2}$ to $X^2\Pi_{3/2}$ at the equilibrium distance is 139.6cm^{-1}. The results for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states are in good agreement with experimental value of $X^2\Pi$ of OH; and the corresponding value for the state $A^2\Sigma^+$ is also given, although it is only in reasonable agreement with the experimental value. With the use of large active space and big basis set, we believe the theoretical results would have a great improvement.

From the relationship curve of the splitting energy interval between $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ with the distance of OH molecule, the SOC perturbation energy for the $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ is lower than 141cm^{-1}, this directly indicates the perturbation approximation of SOC is reasonable.

References

[1] Zhang S Y 2003 *Chin. Phys.* **52** 2290

[2] Ma H T, Bian W S, Zheng S J and Meng L P 2005 *Acta Chim. Sin.* **63** 263 (in Chinese)

[3] Barrow R E 1956 *Ark. Fys. Semin. Trondhein* **11** 281

[4] Ruscic B, Wagner A F and Harding L B 2002 *J. Phys. Chem.* A **106** 2727

[5] Joens J A 2001 *J. Chem. Phys.* **105** 11041

[6] Zhou W, Yuan Y and Zhang J S 2003 *J. Phys. Chem* A **119** 9989

[7] Fedorov D G, Koseki S, Schmidt M W and Gordon M S 2003 *Int. Rev. Phys. Chem* **22** 577

[8] Foldy L L and Wouthuysen S A 1950 *Phys. Rev.* **78** 29

[9] Fedorov D G, Koseki S, Schmidt M W and Gordon M S 2003 *Int. Rev. Phys. Chem.* **22** 551

[10] Møller C and Plesset M S 1934 *Phys. Rev.* **46** 618

[11] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Energy Function* (Beijing: Science Press)

[12] Li Q, Liu X Y, Wang R, Zhu Z H, Fu Y B and Wang X L 2001 *Chin. Phys.* **10** 501

[13] Herzberg G 1957 *Molecular Spectra and Molecular Structure* (New York: D. Van Nostrand Company)

[14] Gurvich L V, Veyts I V and Alcock C B 1989 *Thermodynamic Properties of Individual Substances* Vol 1 (New York: Hemisphere)

[15] Herzberg G and Huber K P 1979 *Molecular Spectra and Molecular Structure* **4** 508

[16] Carlone C and Dalby F W 1969 *Can. J. Phys.* **47** 1945