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Analytical potential energy function for the electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ of O_2^x (x=+1, −1)*

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The splitting of potential energy levels for ground state $X^2\Pi_g$ of O_2^x ($x = +1, -1$) under spin–orbit coupling (SOC) has been calculated by using the spin–orbit (SO) multi-configuration quasi-degenerate perturbation theory (SO-MCQDPT). Their Murrell–Sorbie (M–S) potential functions are gained, and then the spectroscopic constants for electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are derived from the M–S function. The vertical excitation energies for O_2^x ($x = +1, -1$) are $\nu[O_2^{+1}(^2\Pi_{3/2} \rightarrow X^2\Pi_{1/2})]$ =195.652cm^{-1}, and $\nu[O_2^{-1}(^2\Pi_{1/2} \rightarrow X^2\Pi_{3/2})]$ =182.568cm^{-1}, respectively. All the spectroscopic data for electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are given for the first time.

Keywords: O_2^x ($x = +1, -1$), molecular structure and potential function, Murrell–Sorbie function, spin–orbit coupling

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1. Introduction

Spin–orbit coupling (SOC)[1] is a kind of magnetic effect, and in fact, a relativistic effect. It brings about two essential effects. One is the splitting of multiple levels, which refers to the zero–field splitting or fine structure splitting, and the other is the SOC mixing electronic states of different multiplicities, which allows radiant transitions and non-radiant transitions between them. The SOC is important, because the coupling splitting value increases greatly with the growing of nuclear charge.[2,3]

The interaction of O_2^+ with an inorganic molecule and a hydrocarbon molecule can induce the electric charge transfer reaction in the vibration energy level of O_2^+, which is significant for the gas analysis research. O_2^- is much important for human health，and it has the reputation of 'the growth hormone' or 'the air vitamin'. Therefore, O_2^x ($x = +1, -1$) have attracted a lot of interest of researchers. Chandrasekhar *et al* [4] have investigated the potential curves and the spectroscopic data of O_2^x ($x = +1, -1$) by using the coupled cluster calculation including single and double substitutions (CCSD), the quadratic configuration interaction calculation including single and double substitutions (QCISD), the CCSD with triple excitations non–iteratively (CCSD(T)) and the QCISD with a triples contribution to the energy added (QCISD(T)) methods, separately. The vertical excitation energy from $^2\Pi_{1/2}$ to $^2\Pi_{3/2}$ has been obtained by Binkley *et al* through the SO-CASCI method,[5] but there is a large discrepancy between their result and the experimental value. However, up to now, the potential energy curves and spectroscopic constants of the electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ have been little studied.

In this paper, the energy level splitting of the electronic state $X^2\Pi_g$ of O_2^x ($x = +1, -1$) under SOC is theoretically studied by using the Gamess-US, which is based on the SO multi-configuration quasi-degenerate perturbation theory (SOC-MCQDPT). Zhang[6] and Li[7] have adopted this method to calculate the S_2 and OH molecule, and the obtained results conform to the experimental values.

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2. Computation details

2.1. The dissociation limits of the ground states for O_2^x $(x = +1, -1)$

To calculate and describe the full potential function of O_2^x $(x = +1, -1)$, we must determine the possible electronic states and reasonable dissociation limits. O and O^+, which belong to O(3) group, are in their ground states ^3P_g and ^4S_u, respectively. However, O_2^{+1} belongs to $D_{\infty h}$ group. When O reacts with O^+, producing O_2^{+1} ion, the symmetry decreases accordingly. According to its irreducible representation, the O(3) group can be resolved into the $D_{\infty h}$ group as follows:

$$^3P_g \rightarrow {}^3\Sigma_g^- + {}^3\Pi_g, \quad \text{and} \quad {}^4S_u \rightarrow {}^4\Sigma_u^-.$$

In terms of the principle of the atomic and molecular reaction static,[8] the direct product between $O(^3P_g)$ and $O^+(^4S_u)$, $^3P_g \otimes {}^4S_u \rightarrow ({}^3\Sigma_g^- + {}^3\Pi_g) \otimes {}^4\Sigma_u^- \rightarrow {}^{2,4,6}\Sigma_u^+, {}^{2,4,6}\Pi_u$. O_2^{+1}, also has the exchange of the excited energy, so there are other possible electronic states: $^{2,4,6}\Sigma_g^+$, and $^{2,4,6}\Pi_g$. And then we can obtain

$$\begin{aligned} &O(^3P_g) + O^+(^2P_u) \rightarrow \\ &{}^{2,4,6}\Sigma_g^+, {}^{2,4,6}\Sigma_u^+, {}^{2,4,6}\Pi_g, {}^{2,4,6}\Pi_u, \end{aligned} \tag{1}$$

which includes the electronic state $X^2\Pi_g$ of O_2^{+1}. So its reasonable dissociation limit is

$$O_2^{+1}(X^2\Pi_g) \rightarrow O(^3P_g) + O^+(^4S_u). \tag{2}$$

Similarly, the reasonable dissociation limit of the electronic state $X^2\Pi_g$ for O_2^{-1} can be expressed as

$$O_2^{-1}(X^2\Pi_g) \rightarrow O(^3P_g) + O^-(^2P_u). \tag{3}$$

2.2. H^{SO} Operator and SO-MCQDPT method

Since the ordinary theoretical models for molecular calculation come out of the non-relativistic Schrödinger equation, it is reasonable to include spin–orbit (SO) and other relativistic corrections in these models. The SO-MCQDPT is based on single and double excitations from the complete active space (CAS) and the SOC, and it has several advantages over other multi-reference (MR) methods. Firstly, it is more efficient than other MR based methods such as multi-reference configuration interaction (MR-CI) and MR coupled cluster (MR-CC), because it does not require iterations for diagonal equation or solution to linear equations. Secondly, it can obtain the results within a chemical accuracy. Thirdly, it can describe open shells or excited states as well as closed shell ground states in a single framework. The SOC operator adopts the Breit–Pauli SOC operator in the present work, and the Foldy–Wouthuysen transformation is employed for the simplification of the total Hamiltonian.[9] The total Hamiltonian operator H can be expressed as

$$H = H^{SF} + H^{SO}, \tag{4}$$

where H^{SF} is the spin-free Hamiltonian, and H^{SO} is the spin–orbit Hamiltonian.

The well-known non-relativistic Schrödinger operator is

$$\begin{aligned} H^{NR} = &-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i\sum_\alpha Z_\alpha e^2/r_{i\alpha} \\ &+ \sum_i\sum_i e^2/r_{ij} + \sum_\alpha\sum_\beta Z_\alpha Z_\beta e^2/r_{\alpha\beta}. \end{aligned} \tag{5}$$

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

$$H^{MV} = -\frac{\hbar^4}{8c^2m^3}\sum_i \nabla_i^4, \tag{6}$$

$$H^{D} = -\frac{\pi\hbar^2}{2m^2c^2}\left[\sum_i\sum_\alpha Z_\alpha e^2\delta(r_{i\alpha})\right]. \tag{7}$$

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

$$H^{SF} = H^{NR} + H^{MV} + H^{D}. \tag{8}$$

The final term of the H operator is the SOC term, also known as the Breit–Pauli SO operator,

$$\begin{aligned} H^{SO} = &\frac{1}{2m^2c^2}\left[\sum_i\sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}^3}\hat{I}_{i\alpha}\hat{S}_i \right. \\ &\left. - \sum_i\sum_j \frac{e^2}{r_{ij}^3}\hat{I}_{i\alpha}(\hat{S}_i + 2\hat{S}_j)\right], \end{aligned} \tag{9}$$

which contains the terms for both one-electron and two-electron. In these formulas, $\hat{I}$ and $\hat{S}$ are space and spin angular momentum operators, respectively, $\hat{I}_{j\alpha} \equiv (r_i - R_\alpha) \times P_i$, $\hat{I}_{ij} \equiv (r_i - r_\alpha) \times P_i$, the Roman and Greek subscripts denote electrons and nuclei, respectively. The above models are integrated into the Gamess-US[10] procedure.

We have calculated the structure of electronic state $X^2\Pi_g$ under SOC, the spectroscopic parameters and the potential energy functions, separately. The 6-311++g (3df, 2pd) basis set is used for O_2^x $(x = +1, -1)$.

3. Results and discussion

3.1. Oxygen atom

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

From Table 1, it can be seen that the energy levels split due to the SOC, and the ground state ^3P term of the configuration $2S^22P^4$ for O splits into three different J levels, i.e. $^3P_2$,$^3P_1$ and $^3P_0$. Comparing the calculated values with the experimental values in Table 1, we can see that the calculated results are in good agreement with the experimental values, with the Gamess-US used to process the low-lying states. This method will be extended to O_2^x $(x = +1, -1)$ molecular ions in view of this calculated result.

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

configuration	state	J	measurement/cm^{-1}		calculation/cm^{-1}			
			level[11]	interval	level		interval	
$2S^22P^4$	^3P	2	0.0	158.5	0.00		156.3089	155.2077[7]
		1	158.5	68.5	157.3089	155.2077[7]	71.3311	72.1[7]
		0	226.5		228.64	231.13[7]		

3.2. O_2^x $(x = +1, -1)$ molecular ions

For linear molecules under SOC, the coupling of electronic states[12] can be expressed as

$$\Omega = |\Lambda + \Sigma|, \tag{10}$$

where Λ and Σ are orbit and spin angular momenta, respectively. Under the SOC, electronic state $X^2\Pi$ is split into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ for $\Lambda = 1$, and $\Sigma = \pm 1/2$.

The diatomic potential energy function is the foundation of constructing the polyatomic potential energy function in the entire space.[13–19] All the potential energy functions for the splitting of the ground state are least-square fitted as the M–S function[20]

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \tag{11}$$

where $\rho = R - R_e$ with R being the inter-atomic distance, and R_e being its equilibrium distance.

As can be seen from Figs.1 and 2, it is observed that the potential energy function curves each have a minimum, which corresponds to the balance structure for the electronic state $X^2\Pi_g$ of O_2^x $(x = +1, -1)$ under the SOC. The equilibrium distances from O_2^{+1} to the two states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are the same, i.e. $R_e = 0.11065$ nm. Besides, E $(^2\Pi_{1/2})$=–31.13932 a.u., lower than E $(^2\Pi_{3/2})$= −31.13844 a.u., and the equilibrium distances from O_2^{-1} to the two states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are the same, i.e. R_e=0.13441 nm. But E $(^2\Pi_{1/2})$=–31.55396 a.u. that is higher than $E(^2\Pi_{3/2})$= –31.55552 a.u. at the equilibrium distance. It is shown that the $^2\Pi_{1/2}$ is the ground state and the $^2\Pi_{3/2}$ is the first exciting state for O_2^{+1}. However, $^2\Pi_{3/2}$ is the ground state and the $^2\Pi_{1/2}$ is the first exciting state for O_2^{-1}. In terms of the second rule of Hund, the number of electrons in the outermost-shell is less than or equal to that in the half-shell, the smaller the value of J is, the smaller the energy will be. On the contrary, the smaller the value of J is, the bigger the energy will be. Because the electronic configuration is $\sigma^2\pi^4\sigma^2\pi^1$ for the ground state $X^2\Pi_g$ of O_2^{+1}, the number of electrons in the outermost-shell is less than that in the half-shell. But for O_2^{-1}, the electronic configuration is $\sigma^2\pi^4\sigma^2\pi^3$, so the number of electrons in the outermost-shell is larger than that in the half-shell.

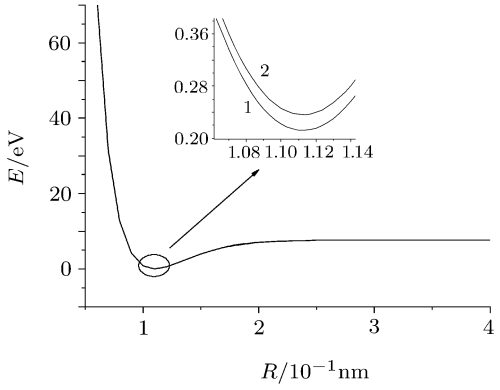


Fig.1. The potential energy curve of the electronic states $X^2\Pi_{1/2}(1)$ and $^2\Pi_{3/2}(2)$ of O_2^{+1}.

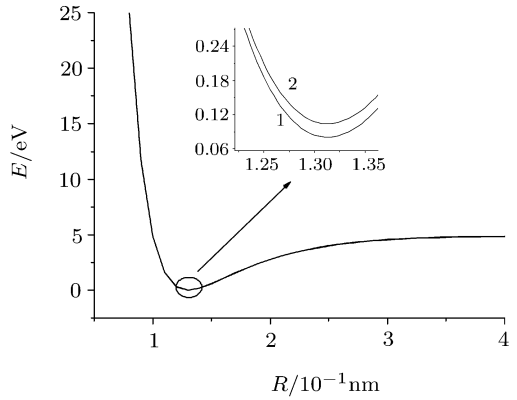


Fig.2. The potential energy curve of the electronic states $X^2\Pi_{3/2}(1)$ and $^2\Pi_{1/2}(2)$ of O_2^{-1}.

The parameters a_1, a_2, a_3, R_e and D_e of the potential energy functions for the corresponding states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are obtained by the least-squares fitting. Comparing the calculated dissociation energy (D_e) and the vertical excitation energy (T_e) with the experimental values in Table 2, we can see that the calculated results are in good agreement with the experimental values. Figures 3 and 4 show the details of the potential energy curves of the electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ for O_2^x ($x = +1, -1$). The results show that the fitting values are close to the calculated data by using the SO-MCQDPT method for O_2^x ($x = +1, -1$).

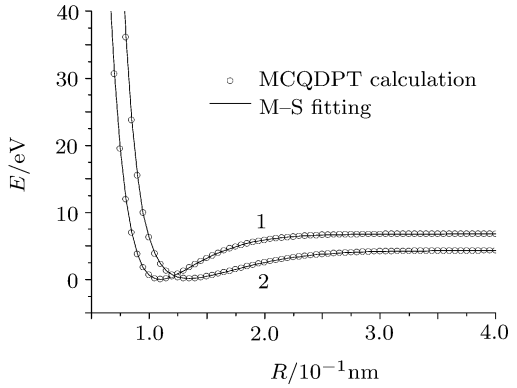


Fig.3. The Murrell–Sorbie potential energy curves of the electronic states $\Pi_{1/2}(O_2^{+1})$ (curve 1) and $\Pi_{3/2}(O_2^{-1})$ (curve 2).

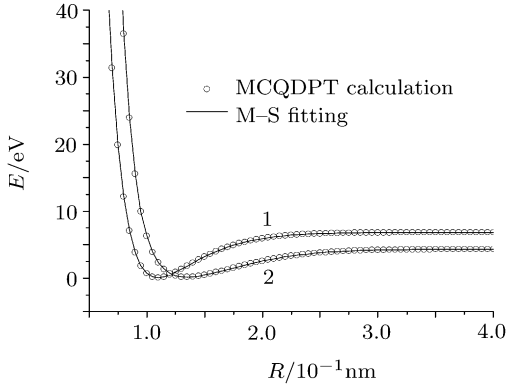


Fig.4. The Murrell–Sorbie potential energy curves of the electronic states $^2\Pi_{3/2}(O_2^{+1})$ (curve 1) and $^2\Pi_{1/2}(O_2^{-1})$ (curve 2).

Table 2. Parameters of Murrell–Sorbie potential functions of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ for O_2^x ($x = +1, -1$).

ion	state		R_e/nm	D_e/cm^{-1}	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	T_e/cm^{-1}
O_2^+	$X^2\Pi_{1/2}$	MCQDPT	0.11065	6.7818	49.448	435.72	3747.7	0
	$^2\Pi_{3/2}$	MCQDPT	0.11065	6.7821	49.208	425.34	3492.76	195.652, 197.3[2], 200.2[21] 155.9[5]
	$X^2\Pi$	Exp.[2]	0.11164	6.7806				
O_2^-	$X^2\Pi_{3/2}$	MCQDPT	0.13441	4.1625	44.8398	570.047	5722.80	0
	$^2\Pi_{1/2}$	MCQDPT	0.13441	4.1627	44.6026	557.199	5572.18	182.568
	$X^2\Pi$	Exp.[2]	0.135	4.1613				

Moreover, it is easy to derive the force constants f_2, f_3 and f_4 from the M–S function, and then calculate the spectroscopic data ω_e, $\omega_e\chi_e$, B_e and α_e. All these data are listed in Tables 3 and 4, respectively. The corresponding formulas are as follows:

$$f_2 = \left.\frac{d^2V}{dr^2}\right|_{r=R_e} = D_e(a_1^2 - 2a_2), \tag{12}$$

$$f_3 = \left.\frac{d^3V}{dr^3}\right|_{r=R_e} = -6D_e(a_3 - a_1a_2 + \frac{1}{3}a_1^3), \tag{13}$$

$$f_4 = \left.\frac{d^4V}{dr^4}\right|_{r=R_e} = D_e(2a_1^4 - 12a_1^2a_2 + 24a_1a_3), \tag{14}$$

$$B_e = \frac{h}{8\pi^2\mu c R_e^2}, \tag{15}$$

$$\alpha_e = -\frac{6Be^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \tag{16}$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \tag{17}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \tag{18}$$

Table 3. Force constants of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ for O_2^x $(x = +1, -1)$.

ion	state		$f_2/(10^2\text{aJ}\cdot\text{nm}^{-2})$	$f_3/(10^3\text{aJ}\cdot\text{nm}^{-3})$	$f_4/(10^4\text{aJ}\cdot\text{nm}^{-4})$
O_2^+	$X^2\Pi_{1/2}$	MCQDPT	17.44487	–124.78483	455.88486
	$^2\Pi_{3/2}$	MCQDPT	17.52436	–125.42533	450.80197
O_2^-	$X^2\Pi_{3/2}$	MCQDPT	5.80562	–40.87040	302.28430
	$^2\Pi_{1/2}$	MCQDPT	5.83575	–41.20541	302.52787

Table 4. Spectroscopic constants of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ for O_2^x $(x = +1, -1)$.

ion	state		ω_e/cm^{-1}	$\omega_e\chi_e/\text{cm}^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}
O_2^+	$X^2\Pi_{1/2}$	MCQDPT	1924.124	15.417	1.70321	0.01482
	$^2\Pi_{3/2}$	MCQDPT	1928.503	15.549	1.70321	0.01480
O_2^-	$X^2\Pi_{3/2}$	MCQDPT	1109.982	8.289	1.20225	0.01683
	$^2\Pi_{1/2}$	MCQDPT	1112.859	8.485	1.20225	0.01686

4. Conclusions

The theoretical research of molecular ion structure for O_2^x $(x = +1, -1)$ under the SOC has been carried out by using the method of SO-MCQDPT in Gamess-US package.

The calculations for the three sublevels $^3P_2$, $^3P_1$ and $^3P_0$ of the ground term ^3P of oxygen atom are in good agreement with the experimental values. These results justify the feasibility of the SO-MCQDPT method. The potential energy curves for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ have been fitted by the least-square fitting with the M–S analytical function, and the relevant spectrum constants (ω_e, $\omega_e\chi_e$, B_e, α_e) of the two states have been obtained for the first time in our research. The vertical excitation energies for O_2^x $(x = +1, -1)$ are in line with the experimental data.

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