Accurate calculation of the potential energy curve and spectroscopic parameters of $X^2\Sigma^+$ state of $^{12}Mg^1H$*

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High level calculations on the ground state of $^{12}Mg^1H$ molecule have been performed using multi-reference configuration interaction (MRCI) method with the Davidson modification. The core–valence correlation and scalar relativistic corrections are included into the present calculations at the same time. The potential energy curve (PEC) of the ground state, all of the vibrational levels and spectroscopic parameters are fitted. The results show that the levels and spectroscopic parameters are in good agreement with the available experimental data. The analytical potential energy function (APEF) is also deduced from the calculated PEC using the Murrell–Sorbie (M–S) potential function. The present results can provide a helpful reference for the future spectroscopic experiments or dynamical calculations of the molecule.

Keywords: multi-reference configuration interaction, potential energy curve, analytical potential energy function, spectroscopic parameters

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1. Introduction

The MgH molecule has gained great attention in the astrophysical community in the past quarter century.[1] The visible emission of MgH was first observed in the sun, and it was then observed in many stars. Its quantitative observation was of practical interest as a probe of the relative abundances of magnesium isotopes in stellar atmospheres.[2,3]

In the past few years, there have been quite a lot of studies of MgH molecule. In experiment, the far infrared spectra of magnesium hydride were measured by Leopold *et al.*[4] in 1986, who observed that the transitions can be reproduced within 1 MHz. Lemoine *et al.*[5] investigated the infrared diode laser spectra of MgH in 1988 and obtained some spectral lines of the transition band. Shayesteh *et al.*[6] observed several vibration–rotation bands and obtained 0–4 levels, equilibrium bond distances, vibrational and rotational constants of MgH in 2004. Later, they used a Fourier transform spectrometer to measure the visible emission spectra of the MgH molecule and gained 0–10 levels and several spectroscopic parameters in 2007.[3] With respect to theoretical study, MgH is quite a simple molecule with three valence electrons, a ground state, and several excited states, and has been studied using *ab initio* all-electron calculations during the 1970s. The vertical excitation energies of MgH were calculated using the multi-reference single and double configuration interaction method (MRDCI) by Bruna and Grein.[7] Mestdagh *et al.*[8] in 2009 investigated the potential energy curves (PECs) and molecular constants for all MgH from ground states up to the excited atomic configurations Mg ($3s3d\,^1D$) + H ($1s^2S$), and these calculations help to clarify the very complicated spectrum of MgH in the 3.5×10^4 cm^1–4.6×10^4 cm^1 excitation range. In 2012, Mostafanejad and Shayesteh[9] calculated the PECs and transition dipole moments of MgH using multi-reference configuration interaction method with large active space and basis sets. In 2013, using the direct-potential-fit method, Henderson *et al.*[10] obtained an accurate PEC for the ground state that reproduces all the observed rovibrational energy levels within their experimental uncertainties of 0.005 cm^{-1}. There are some differences of energy levels and spectroscopic parameters from their experiment data, which may be caused because they did not take into consideration the core–valence correlation and scalar relativistic influence. Therefore, to improve the quality of spectroscopic parameters of the MgH radical, more accurate calculations should be performed.

In the present work, the PEC of ground state is calculated by the high-level *ab initio* configuration interaction method, which is extrapolated to the complete basis set (CBS) limit. In order to obtain the accurate PEC, the core–valence correlation and scalar relativistic corrections are also taken into account in our calculations. The spectroscopic parameters are determined from the calculated PEC. Finally, we fit the PEC into the analytical potential energy function (APEF) by us-

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ing the Murrell–Sorbie (M–S)[11–15] potential function, and determine the spectroscopic parameters by using the obtained APEF. These provide a convenient expression to build an analytical potential energy surface of the polyatomic system or to study the dynamics of the photo dissociation and photo association of the molecule.

2. Computational method

2.1. Technical details for the calculations of PEC

In the present study, the electronic structure calculations are carried out with the Molpro2010.1 site of the quantum chemical package designed by Werner *et al.*[16] The symmetry point group of MgH is $C_{\infty v}$, owing to the limitation of the Molpro program, all of the calculations are performed in the C_{2v} subgroup of the $C_{\infty v}$ point group. The corresponding relationships between the irreducible representations of the C_{2v} and $C_{\infty v}$ point groups are $\Sigma^+ = A_1$, $\Pi = B_1 + B_2$, $\Delta = A_1 + A_2$, and $\Sigma^- = A_2$. The state-averaged complete active space self-consistent field (CASSCF)[17,18] approach is used to calculate the energies of the ground state of MgH, where the active space includes 3s3p atomic orbitals (AO) on a Mg atom and 1s AO on a H atom. Further, by utilizing the CASSCF energies as reference values, the energies of the ground state are computed with the internally contracted multireference configuration interaction (MRCI)[19,20] method, including Davison correction (MRCI + Q),[21] which has been used for many diatomic molecules.[22–26] The inner-shell $1s^2$ electrons of Mg are kept frozen, while the $2s^22p^6$ electrons of Mg are correlated to account for the core–valence correlation. That is to say, a total of 11 electrons in MgH (excluding $1s^2$ electrons of Mg) are correlated in the MRCI + Q calculations.

To improve the quality of the spectroscopic parameters, the core–valence correlation and scalar relativistic corrections are considered in the PEC calculations. In this work, core–valence correlation correction is included with a ccpCVTZ[27] basis set at the level of MRCI + Q theory, and its contribution is denoted as CV. Scalar relativistic correction is taken into account via the third-order Douglas–Kroll Hamiltonian (DKH3)[28,29] approximation at the level of a cc-pVTZ basis set, and its contribution is denoted as DK. Here, the core–valence correlation and scalar relativistic corrections are applied across the entire PEC.

Three correlation-consistent basis sets: aug-cc-pVTZ (AVTZ) (AVQZ) and AV5Z,[30,31] are used for the present extrapolation scheme (denoted as Q5). The extrapolation formula is written as[32]

$$E(n) = E_{\rm CBS} + a \times \exp(-cn), \tag{1}$$

$$E(n) = E_{\rm CBS} + b \times \left(n + \frac{1}{2}\right)^{-3}. \tag{2}$$

Here, $E(n)$ is the total energies obtained by the basis sets AVnZ (n = 3, 4, 5), $E_{\rm CBS}$ is the total energy extrapolated to the CBS limit a, b, and c are the fitted parameters.

2.2. Vibrational levels

The rotational and vibrational energy levels are determined by solving the Schrödinger equation of nuclear motion with the *ab initio* PEC, these calculations are carried out with the LEVEL 8.0 program package[33]

$$\begin{aligned} E(v,J) &= G(v) + B_v[J(J+1)] - D_v[J(J+1)]^2 \\ &\quad + H_v[J(J+1)]^3 + \cdots. \end{aligned} \tag{3}$$

Here, v is the vibrational quantum number and J represents the rotational quantum number, $G(v)$ is the vibrational level, B_v is the internal rotation constant, D_v and H_v are the first two centrifugal distortion constants.

2.3. Analytical potential energy function and spectroscopic parameters

The M-S function suggested by Murrell *et al.*[34] can be used to represent the two- and three-body terms of the potential energy surface.[35,36] Here, we use the two-body term to express the interaction between Mg and H atoms. The expression is written as

$$V(\rho) = -D_{\rm e}\left(1 + \sum_{i=1}^{n} a_i \rho^i\right)\exp(-a_1\rho), \tag{4}$$

where $\rho = R - R_{\rm e}$, with R and $R_{\rm e}$ being the internuclear distance and equilibrium bond length, respectively, $D_{\rm e}$ is the dissociation energy, a_i and $D_{\rm e}$ are the parameters that can be determined by fitting. After trying a series of fittings, we find that the reasonable APEF of the ground state MgH molecule can be obtained when n equals 10. The root-mean-square (RMS) error can be used to assess quantitatively the quality of the fitting. The RMS can be calculated from

$$RMS = \frac{1}{N}\sqrt{\sum_{i=1}^{N}(V_{\rm APEF} - V_{ab\ initio})^2}, \tag{5}$$

where $V_{\rm APEF}$ and $V_{ab\ initio}$ are the energies given by the fitting and the *ab initio* calculations, respectively, and N is the number of energy points to be used in the fitting.

Based on the relationship equations among spectroscopic parameters and APEF, the spectroscopic parameters can be calculated. Furthermore, the precision and credibility of the APEF can be testified by directly comparing the calculated spectroscopic parameters with experimental data. First of all, the force constants can be determined from the parameters of M-S potential energy function as[37]

$$\begin{aligned} f_2 &= D_{\rm e}(a_1^2 - 2a_2), \\ f_3 &= 6D_{\rm e}\left(a_1a_2 - a_3 - \frac{a_1^3}{3}\right), \\ f_4 &= D_{\rm e}(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \end{aligned} \tag{6}$$

where f_2, f_3, and f_4 are quadratic, cubic, and quartic force constants, respectively. Then the spectroscopic parameters are[37]

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad \omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \tag{7}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1+\frac{f_3 R_e}{3f_2}\right), \tag{8}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4 R_e^2}{f_2}+15\left(1+\frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \tag{9}$$

Here B_e is the rigid-rotational factor, α_e is the nonrigid-rotational factor, ω_e is the harmonic vibrational frequency, and $\omega_e\chi_e$ is the inharmonic vibrational factor.

3. Results and discussion

3.1. PEC of $X^2\Sigma^+$ state

Using the MRCI+Q method and different correlation-consistent basis sets, we calculate the PEC of the $X^2\Sigma^+$ state for internuclear separations from about 1.2 Å to 6.05 Å in steps of 0.05 Å, except near the internuclear equilibrium position. A smaller step is adopted near the internuclear equilibrium position so that the properties of each PEC can be displayed more clearly. In the above calculation, the core–valence correlation and scalar relativistic corrections have been taken into account. The spectroscopic parameters (R_e, D_e, and ω_e) are listed in Table 1. As demonstrated in Table 1, we can see that the R_e, D_e, and ω_e values will change as the basis sets change. The differences in R_e between the calculated results and experimental data are 0.0163, 0.0133, 0.0103, and 0.0088 Å. The values of D_e are 0.0181, 0.0407, 0.0499, and 0.0597 eV, and the values of ω_e are 7.99, 5.79, 4.51, and 1.43 cm^{-1} at the AVTZ, AVQZ, and AV5Z basis sets and the CBS limit, respectively. From the differences in R_e, D_e, and ω_e, we find that the errors become smaller as the basis set increases except D_e. In conclusion, we think that the present calculations at the CBS limit are close to the experimental results. Consequently, we use the PECs determined by the MRCI + Q approach and extrapolation to the CBS limit for the present spectroscopic calculations.

Table 1. Equilibrium parameters of $^{12}Mg^1H$ with different basis sets.

Basis sets	R_e/Å	D_e/eV	ω_e/cm^{-1}
AVTZ-CV-DK	1.7384	1.3949	1487.21
AVQZ-CV-DK	1.7233	1.4175	1489.41
AV5Z-CV-DK	1.7271	1.4267	1490.69
Q5-CV-DK	1.7293	1.4365	1496.63
Exp.[38]	1.729682	1.3768	1495.20

3.2. Vibrational energy levels

Based on the obtained PEC, we solve the one-dimensional Schrödinger equation of nuclear motion with the LEVEL 8.0 program package. For brevity, we collect and list the lower 11 bound vibrational levels of the $X^2\Sigma^+$ ground state but omit the rotational levels in Table 2. It is found that the present computed vibrational levels and rotational constants are both in agreement with the available experimental data in the literature.[3] The least difference is 1.80 cm^{-1} ($v = 6$), the largest deviation is 348.43 cm^{-1} ($v = 10$). The reason for this is probably the anharmonic vibration. When v increases, the anharmonic vibration becomes more obvious. But the average percent error of vibrational levels is only 0.43%, which implies that the predicted levels are reliable. This is a helpful reference for future theoretical or experimental investigations.

Table 2. Vibrational levels and rotational constants for the $X^2\Sigma^+$ state of $^{12}Mg^1H$ (in units of cm^{-1}).

v	T_v		B_v	
	This work	Exp.[3]	This work	Exp.[3]
0	732.2507	739.1094	5.681111	5.736508
1	2159.8113	2171.0874	5.506157	5.555289
2	3526.7556	3539.7878	5.325048	5.367551
3	4829.6412	4841.4399	5.134570	5.169787
4	6063.4007	6070.4989	4.929697	4.956644
5	7220.5652	7218.7623	4.702485	4.719638
6	8290.1023	8273.9182	4.441160	4.444650
7	9257.6102	9217.1113	4.139117	4.106852
8	10116.3692	10018.7619	3.822747	3.659651
9	10850.3306	10631.8328	3.326479	3.007412
10	11336.9351	10988.5015	2.474851	1.968707

3.3. Analytical potential energy function and spectroscopic parameters

To make the PEC more convenient for further applications, we construct APEF for the ground state of MgH with the M–S potential. The fitted parameters and RMS are presented in Table 3, and the fitted PEC are plotted in Fig. 1. As seen in Table 3, the RMS is only 0.004519 eV, which implies that the fitting process is of high quality and the present APEF can accurately reproduce the interaction energy between Mg and H atoms. From Fig. 1, the satisfactory fitting results also suggest that the M–S potential can effectively reproduce the short-range PEC. At the same time, we calculate the spectroscopic parameters with the APEF, and the results are listed in Table 4. From Table 4, it is found that some of spectroscopic parameters obtained by M–S potential are closer to experimental value than other theoretical data except D_e, which again shows the accuracy of the present calculations. The value of R_e is 1.7293 Å, which is very close to the experimental value of 1.7297 Å, and the relative error is only 0.023%. The dissociation energy D_e differs from the experimental value by 0.0597 eV. The error is a little bigger than the other theoretical value, which may be the reason for the basis set extrapolation and no consideration of the spin orbit coupling. The

Table 3. M–S APEF parameters for the $X^2\Sigma^+$ state of $^{12}Mg^1H$ and RMS.

D_e/eV	R_e/Å	a_1/Å^{-1}	a_2/Å^{-2}	a_3/Å^{-3}	a_4/Å^{-4}	RMS/eV
1.4365	1.7293	3.202489	2.352124	0.420700	−0.380129	0.004519
a_5/Å^{-5}	a_6/Å^{-6}	a_7/Å^{-7}	a_8/Å^{-8}	a_9/Å^{-9}	a_{10}/Å^{-10}	
–3.275059	–0.425492	3.609798	–2.185833	0.513923	–0.043316	

Table 4. Comparisons between spectroscopic parameters and available experiment and other theoretical results for the $X^2\Sigma^+$ state of $^{12}Mg^1H$.

	D_e/eV	ω_e/cm^{-1}	R_e/Å	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
M–S fit.	1.4365	1496.63	1.7293	32.061	5.8284	0.1895
Ref. [8]	1.3613	1453.7	1.72	29.4	–	–
Ref. [9]	1.3826	1491.6	1.741	31.0	–	–
Ref. [40]	1.3850	1484.4	1.743	30.989	5.7177	0.1453
Ref. [41]	1.4344	1485.6	1.7933	28.9	–	–
Exp. [39]	1.3768	1495.20	1.7297	31.889	5.8257	0.1859

fitted ω_e is 1496.63 cm^{-1}, which is closer to the experimental value 1495.20 cm^{-1} than the other results, the difference is only 1.43 cm^{-1}. Both $\omega_e\chi_e$ and B_e accord with the experimental value, with the relative errors being 0.539% and 0.046%, respectively. This implies that the theoretical level MRCI + Q/Q5 + CV + DK can give accurate results for both the spectroscopic and potential energy properties of the MgH molecule.

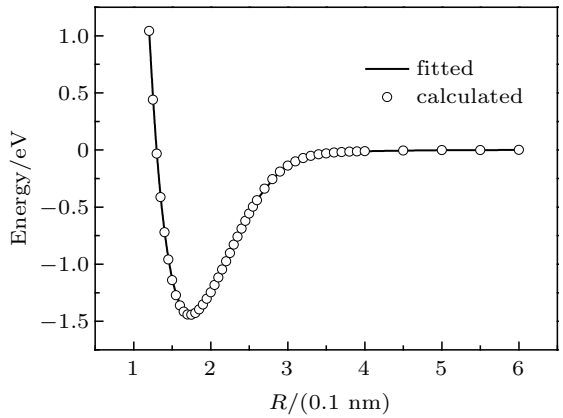


Fig. 1. Fitted and calculated potential energy functions for $X^2\Sigma^+$ state of $^{12}Mg^1H$.

4. Conclusion

In this work, the PEC of $X^2\Sigma^+$ state of the $^{12}Mg^1H$ molecule are obtained at an MRCI + Q/Q5 + CV + DK theoretical level. The vibrational levels and the spectroscopic parameters are determined. It is found that the computational vibrational levels for the $X^2\Sigma^+$ state of the $^{12}Mg^1H$ molecule are in good agreement with the theoretical ones. In addition, most of the fitted spectroscopic parameters are in accordance with the experimental data. The M–S potential can accurately reproduce the present short-range PEC, which is important for understanding not only the significant chemical processes in molecular clouds in astrophysics but also the relation to the composition of the molecular dissociation process. The accurate APEF can be conveniently used for investigating the photo association transition or the construction of APEF for a polyatomic system.

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