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THEORETICAL INVESTIGATION OF THE ELECTRONIC STRUCTURE AND SPECTRA OF ALKALINE-EARTH RARE-GAS COMPLEXES BeHe MOLECULE

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Abstract

We present a study of an Ab initio quantum chemistry of alkaline earth rare gas system (BeHe) molecule. Our study is based on the use of pseudopotential techniques and core polarization potentials. Our system is handled with two active valence electrons taking interest of the zero pseudopotential approach for He. We determine the potential energy curves of 24 states of $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetries, and their spectroscopic parameters $(R_e, D_e, \omega_e, \ \omega_e\chi_e, T_e$ and $B_e)$, and obtain a good agreement with available works. However, many excited states for BeHe are treated for the first time. The transition and permanent dipole moments curves are determined for the 1, $^3\Sigma^+$ states of the BeHe in a large range of R.

1. Introduction

The alkaline earth rare gas diatomic molecules present weakly bound potentials and we need more information about the interatomic potential between a helium atom and an alkaline-earth atom to understand for example the sympathetic cooling in Bose condensates and many other phenomena. Hence, this system has attracted many teams of theoretical and experimental workers.

Several theoretical [1-18] and experimental [19-23] studies have been performed for alkaline-earth/alkali-rare gas molecule. Hliwa et al. [1] were the first to study these systems, they calculated the potentials curves of the Mg-Ar system by using pseudopotentials models. In the same context Stwalley [2] and Hyman [3] have estimated the van der Waals constants of alkali-rare gas systems. By using the potential model, of Böttcher et al. [4] and Malvern [5] have studied the potential curves for excited states of CaHe, CaNe, MgHe and MaNe systems. Schwerdtfeger et al. [6] used ab initio and pseudopotential models to determine the potentials curves for MgAr, SrAr, BaAr and CaAr systems. Later Czuchaj et al. [7] using pseudopotential they have analyzed the interaction between (M = Mg, Cd, Hg) and (He, Ne) atoms. On the other hand, Chalasinski and Simons [8] have studied the $^{3}\pi$ state of MgHe by using the Møller-Plesset perturbation. In another paper, Funk et al. [9] applied the ab initio calculations of interaction between alkaline-earth atoms with the rare-gas atoms by Møller-Plesset perturbation for MgHe system, to obtain the ground state potentials find out more information about the well region. Chiles and Dykstra [10] they have used the approximation of double-substituted coupled-cluster and coupled-electron pair calculations for MgHe system to determine the minimum parameters for the potentials. In addition, Stienkemeier et al. [11] evaluated the CaHe and SrHe systems by using multi-reference configuration interaction. In references [12] and [13, 14], the repulsive region for the states of CaHe and BaHe, respectively, have been determined. The Fock damped dispersion was applied by Reho et al. [15], to calculate the potentials for MgHe and CaHe. Also, the potentials states for the BeHe system have been a topic of interest to Leung and Breckenridge [16] who used Møller-Plesset perturbation. The surface integral method was utilized by Kleinekathöfer [17] to conclude the ground state potentials for BeHe, MgHe, CaHe, SrHe and BaHe systems. Similarly, Lovallo and Klobukowski [18] investigated the same system with CCSD(T) level of theory, they found a single bound vibrational state for each complex, they report that Mg and Be exist inside a helium nanodroplet while the Ca and Sr should occupy the dimple on the surface and Ba occupying the surface sites.

Experimentally some teams studied the alkaline earth rare gas molecules, for example Kowalski et al. [19]. Besides, Toennies and Vilesov [20] have studied the helium clusters doped by chromophore molecules and atoms. Many other systems are studied and their spectrum has been determined like XMg [21], XCa, XSr [22], XBa [23] with X represent the alkaline-earth metals but the binding energy of the alkaline-earth atoms to the cluster is not completely investigated.

Most of these types of physical phenomena are described in mathematical formulae as systems of differential equations as mentioned in [24-26].

The structure of this paper is: the computational methodology is presented in Section 2. In Section 3, the potential energy curves and their spectroscopic parameters for 24 states of $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetries are presented and compared with available results. Additionally we presented and analyzed the spectra of permanent and transition dipole moments. We summarize and conclude the work in Section 4.

2. Method of Calculation

We have used ab initio quantum chemistry computational techniques involving a non-empirical pseudopotential method to calculate the adiabatic potentials energies for BeHe molecule. The number of valence electrons of the alkaline-earth/rare gaz BeHe system has been restricted to two electrons by using pseudopotentials of Durand and Barthelat [27]. Furthermore, the SCF techniques are accompanied by a full valence CI calculation employing the package codes (CIPSI, MOYEN, BDAV) of the Laboratoire de Physique et Chimie Quantique of Toulouse, used in our previously works [28-33]. The correlation core valence is taken account using the operator formalism of Muller et al. [34], CPP (core polarization potential), written like this:

$$W_{CPP} = -\frac{1}{2}\sum_{\lambda} \alpha_\lambda \vec{f}_\lambda \vec{f}_\lambda \qquad (1)$$

α_λ is the electric dipole polarizability (EDP) of atomic core λ.

$\vec{f}_\lambda$ is the electric field created at center λ produced by the valence electrons and all other cores.

For beryllium core: EDP is $\alpha_{\mathrm{Be}} = 0.052\ a_0^3$ [35], the contracted basis is 7s/8p/9d and the cut-off radius is 1.013 a.u. For helium core: EDP is $\alpha_{\mathrm{He}} = 1.3834\ a_0^3$ [36], the uncontracted basis is 3s/2p [37] and the cut-off radius is 1.50 a.u. It is essential to use a basis set for He atom to treat the steric distortion of the Be valence orbitals obtaining from their orthogonality with the rare-gas closed shells that are represented by the pseudo-potential. Because no active electrons on the helium atom, the exponents were calculated in order to provide correct overlap with the 3s/2p orbitals of He, and to extend toward the diffuse range.

In Table 1, we presented the atomic energy levels of ground and many excited states of Be atom and we compared them with the work of Moore [38]. The maximum absolute errors do not exceed 517 cm^{-1}.

Table 1. Neutral beryllium energy levels spectrum $(E_{Be} - E_{Be^+})$ in cm^{-1} and the error of this work compared to the work of Moore [38]

Atomic levels	This work	Exp [38]	$\lvert \Delta E \rvert$
$^1S(2s^2)$	–222590.66	–222073.58	517.08
$^1S(2s2p)$	–178998.76	–179508.60	509.84
$^1S(2s3s)$	–167471.27	–167393.58	77.69
$^1S(2p^2)$	–165146.37	–165637.78	491.40
$^1S(2s3p)$	–161744.07	–161827.69	83.61
$^3S(2s2p)$	–200490.85	–200095.35	395.49
$^3S(2s3s)$	–169981.19	–169983.38	2.194
$^3S(2s3p)$	–163208.85	–163289.4	80.54
$^1P(2s2p)$	–178998.76	–179508.60	509.84
$^1P(2p^2)$	–165146.37	–165637.78	491.40
$^1P(2s3p)$	–161744.07	–161827.69	83.61
$^1P(2s3d)$	–157431.17	–157646.69	215.52
$^3P(2s2p)$	–200490.85	–200095.35	395.49
$^3P(2s3p)$	–163208.85	–163289.4	80.54
$^3P(2s3d)$	–162238.55	–162317.12	78.57
$^3P(2p^2)$	–159681.01	–160022.07	342.38
$^1D(2p^2)$	–165146.37	–165637.78	491.40
$^1D(2s3d)$	–157431.17	–157646.69	215.52
$^3D(2s3d)$	–159679.69	–160022.07	342.38

To calculate the BeHe energy we need to $Be^{2+}He$ and Be^+ potentials energies determined previously in our group [39]. The Be^+He potential is obtained using the interaction between Be^{2+} and the He atom, and the $Be^{2+}He$ potential is obtained using CCSD(T) calculations with Molpro program.

3. Results and Discussion

3.1. Potential energy curves and spectroscopic constants

The PECs for the ground and excited states are determined for an intermolecular distance from 2.0 to 150 a.u. for BeHe systems. To verify the precision of our potential energy curves we have extracted the spectroscopic parameters and compared them with the available theoretical works (see Table 2).

Table 2. Spectroscopic constant for the Σ^+, Π, and Δ states of BeHe molecules (R_e in atomic units, D_e, T_e, ω_e, $\omega_e\chi_e$ and B_e in cm^{-1})

States	R_e	D_e	T_e	ω_e	$\omega_e\chi_e$	B_e
$1^1\Sigma^+$	8.65	6		16.43	9.18	0.28
	8.78[a]	5.7[a]		13.8[a]		
	7.98[b]	8.22[b]				
	9.14[g]	4.64[g]				
	8.99[c]					
	8.95[d]					
	8.71[e]					
$2^1\Sigma^+$	2.65	–7211	50883	956.93	38.10	3.101167
2nd	14.43	6	43665	8.67		
$3^1\Sigma^+$	2.64	2253	52605	865.03	58.80	3.115464
$4^1\Sigma^+$	3.91	2178	55585	823.71	850.66	1.397113
$5^1\Sigma^+$	2.86	–1029	61760	537.34	159.29	2.638496
2nd	4.37	1146	59585	2743.44		
$6^1\Sigma^+$	2.77	295	64727	732.10	80.27	2.826022
2nd	4.37	1364	63658	1963.73		
3rd	5.70	–84	65106	232.66		
$1^3\Sigma^+$	2.67	–28985	51458	839.76	70.92	3.042460

2nd	10.26	26	22447	13.90		
$2^3\Sigma^+$	3.47	–846	53093	676.58	236.27	1.791242
$3^3\Sigma^+$	3.07	452	58721	872.99	213.90	2.292784
$4^3\Sigma^+$	4.71	–1246	63869	214.29	91.436	2.964320
$5^3\Sigma^+$	3.20	–399	65947	589.90	188.49	2.102069
2nd	5.12	–282	65830	144.81		
$6^3\Sigma^+$	2.80	–2151	70886	803.37	44.99	2.770910
2nd	5.81	–1483	70218	128.73		
3rd	11.29	7	68727	97.05		
$1^1\Pi$	2.80	2340	41331	775.62	43.06	2.767127
2nd	6.46	154	43518	67.57		
$2^1\Pi$	2.78	–1249	59012	723.47	61.59	2.812171
2nd	9.73	36	57727			
$3^1\Pi$	3.35	–2296	63027	397.30	340.6	2.087697
2nd	6.17	203	60529	95.35		
$4^1\Pi$	2.81	–3539	68561	590.49	114.49	2.738546
2nd	6.45	200	64822	82.57		
$1^3\Pi$	5.78	260	22214	92.07	9.01	0.649829
	7.18[a]	12[a]		24[a]		
$2^3\Pi$	2.78	1320	57853	712.53	62.91	2.817036
2nd	5.19	466	58707	125.74		
$3^3\Pi$	2.92	–1746	62836	463.66	138.27	2.519986
2nd	10.30	30	61060	19.59		
$4^3\Pi$	2.80	–5431	68053	659.19	77.21	2.762403
2nd	6.31	269	62354	190.92		
$5^3\Pi$	2.82	-2556	71291	640.09		
2nd	5.32	449	68286	127.56		
$1^1\Delta$	7.88	68.76	72	146	–93.92	0.348382
$2^1\Delta$	2.65	–7211	50883	956.93	38.10	3.101167
$1^3\Delta$	2.85	519	62104	604.74	91.45	2.666762
2nd	5.24	486	62137	134.04		

[a] QCISD(T) from Reference [16].

[b] Surface integral from Reference [17].

[c] MP2, [d] CCSD and [e] CCSD(T) method from Reference [18].

[g] ACCD from Reference [10].

We have determined 24 lowest electronic states of $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetries of BeHe neutral molecule. The PECs are drawn in Figures 1 and 2 for $^1\Sigma^+$ and $^3\Sigma^+$ electronic states. Figures 3, 4 and 5 present, respectively, the $^1\Pi$, $^3\Pi$ and $^{1,3}\Delta$ electronic states. Most of the curves are smooth and sometimes we observe repulsive states. Most of curves are smooth with well-defined unique minimum peculiarly for the very low states. A very important behavior due to undulating of atomic Rydberg orbitals in higher excited electronic states, provides a double and a triple well barriers. We observe also in the higher excited states many avoided crossings that have an important significance for the excitation of charge transfer efficiency, for example $2^1\Sigma^+$-$3^1\Sigma^+$ around 4 a.u position. We derive the spectroscopic parameters $(R_e, D_e, T_e, \omega_e, \omega_e\chi_e$ and $B_e)$ for all electronic states which have been analyzed and compared with works in [10, 16-18]. We observed an excellent agreement between our equilibrium distance (R_e), dissociation energy (D_e) and the harmonic frequency (ω_e) and those of available works for the ground $^1\Sigma^+$ state. Our value of R_e is equal to 8.65 a.u, which differs only by 0.06 a.u, 0.13 a.u and 0.49 with the value obtained by Lovallo and Klobukowski [18], Leung and Breckenridge [16] and Chiles and Dykstra [10], respectively. We observe also this excellent agreement for D_e. The difference of the theoretical value is about 0.3 cm^{-1}, 1.35 cm^{-1} and 2.22 $cm4^{-1}$ with the theoretical value of Leung and Breckenridge [16], Chiles and Dykstra [10] and Kleinekathöfer [17], respectively. Our vibrational frequency for the ground state $\omega_e = 16.43\,\mathrm{cm}^{-1}$ is in good accord with that of Leung and Breckenridge [16], they found, 13.8 cm^{-1}. For the 1 $^3\Pi$ state our calculated values are $R_e = 5.78$ a.u, $D_e = 260\,\mathrm{cm}^{-1}$, $\omega_e = 92.07\,\mathrm{cm}^{-1}$ and the values of Leung and Breckenridge [16] are $R_e = 7.18\,\mathrm{cm}^{-1}$, $T_e = 12\,\mathrm{cm}^{-1}$, $\omega_e = 24\,\mathrm{cm}^{-1}$. Therefore, the other spectroscopic constants presented in this work for $^1\Sigma^+$, $^1\Pi$, and $^{1,3}\Delta$ states, studied for the first time. To our knowledge, no experimental studies for the ground and higher excited for BeHe molecule exist.

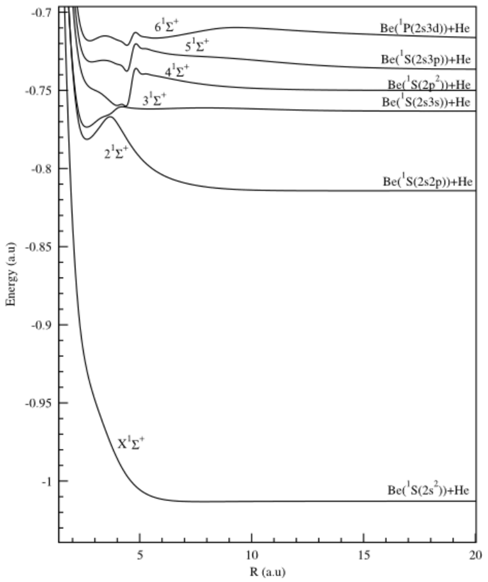

Figure 1. Potential energy curves for the six lowest $^1\Sigma^+$ states of BeHe.

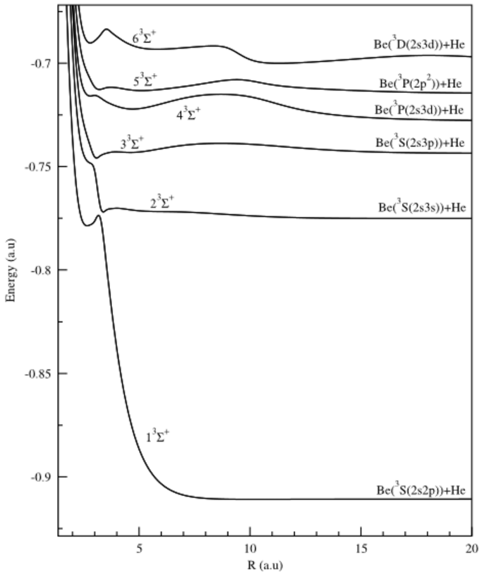

Figure 2. Potential energy curves for the six lowest $^3\Sigma^+$ states of BeHe.

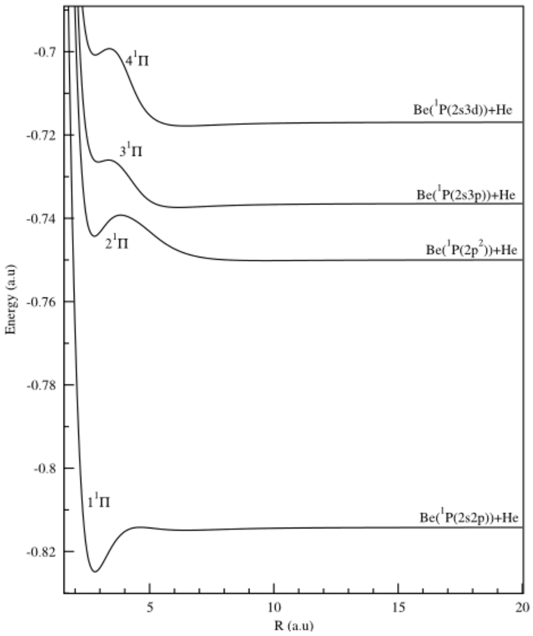

Figure 3. Potential energy curves for the four lowest $^1\Pi$ states of BeHe.

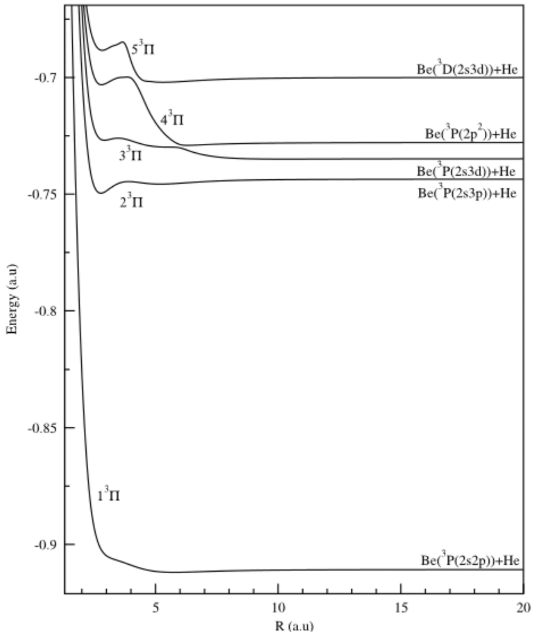

Figure 4. Potential energy curves for the five lowest $^3\Pi$ states of BeHe.

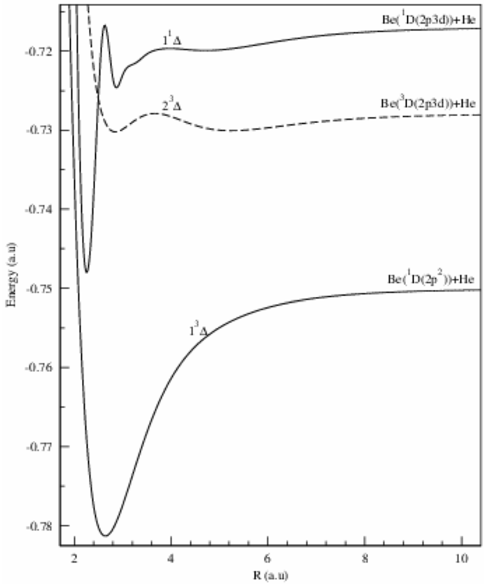

Figure 5. BeHe potential energy curves for the $^1\Delta$ (solid lines) and the $^3\Delta$ (dashed lines).

3.2. Permanent and transition dipole moments for BeHe

To test the accuracy of electronic wave functions and calculated energies, we determined the dipole moment. For this aim, we have calculated the permanent and transition dipole moments for internuclear distances varying from 2.0 to 150 a.u. The permanent dipole moments of the first six $^1\Sigma^+$ symmetries for BeHe, have been calculated which are displayed in Figure 6. We remark that the dipole moment of all states has a maxima located between 6.0 a.u and 14 a.u. Afterwards, it tends towards zero. We note that the $2^1\Sigma^+$ state has the larger dipole moment located at 7.25 a.u. The transition dipole moments between neighbor $^1\Sigma^+$ states have been calculated which are plotted in Figure 7, to better understand the role of the avoided crossings. We note a peak closely to avoid crossings position. We observe for $4^1\Sigma^+$-$5^1\Sigma^+$ and $5^1\Sigma^+$-$6^1\Sigma^+$ transition dipole moments, peaks at 0.133 a.u. and 0.021 a.u. lying at the internuclear distance of 3.37 a.u. and 4.59 a.u, respectively. At a large internuclear distance they vanish, except the

$2^1\Sigma^+$-$3^1\Sigma^+$ transition which reaches a constant of 0.1813 a.u. corresponding to a pure atomic transition between Be($2s^2$)+He and Be(2s3s)+He. Other transition moments tend to zero at large distance.

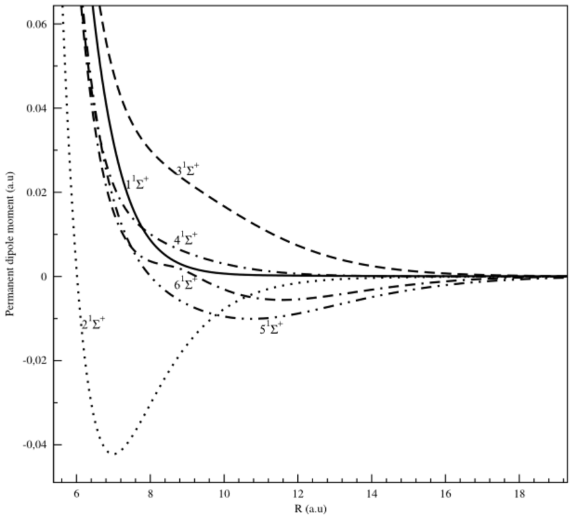

Figure 6. Permanent dipole moment of the first six $^1\Sigma^+$ states of BeHe.

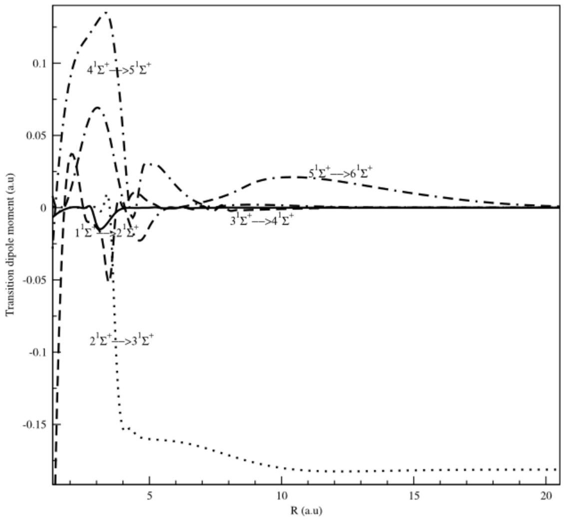

Figure 7. Transition dipole moment between neighbor states of $^1\Sigma^+$ symmetry.

4. Conclusion

In summary, we have performed an *ab initio* study for 24 electronic states of $^{1,3}\Sigma^{+}$, $^{1,3}\Pi$, and $^{1,3}\Delta$ symmetries of the BeHe system. We have used pseudopotential techniques, core polarization potentials and full valence CI calculations to reduce the system to two electrons. For our CCSD (T) calculation we have taken the core-core $\mathrm{Be}^{2+}\mathrm{He}$ potential interactions. The PECs have calculated internuclear distances from 2 to 150 a.u. Moreover, we have extracted and compared the spectroscopic parameters of the (1-6) $^{1,3}\Sigma^{+}$, (1-4) $^{1}\Pi$, (1-5) $^{3}\Pi$, (1-2) $^{1}\Delta$ and 1 $^{3}\Delta$ electronic states. A good concordance with available data in the literature [10, 16-18]. We have calculated most of the excited states for the first time. These electronic states possess important behavior due to undulating of atomic Rydberg orbitals given a double and a triple well barriers. To our best knowledge, in the literature, there is no experimental study on the BeHe for any states. The comparison of the PECs for the BeHe molecule clearly shows the repulsive character of the electron-helium interaction, particularly, in $^{1,3}\Sigma$ symmetries when orbitals along the molecular axis are involved. The permanent and transition dipole moments for BeHe have been obtained, which show many peaks closely to avoid crossings position. We have also determined the transition dipole moments between neighbor $^{1}\Sigma$ symmetric states.

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